NEW REDUCTION METHODS

IN

VOLUMETRIC ANALYSIS

E. KNECHT

AND

E. HIBBERT

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A MONOGRAPH

BY

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PREFACE

THE first attempts to employ titanous chloride as a reducing agent in volumetric analysis were made about nine years ago, and resulted in the successful application of this reagent for the volumetric estimation of ferric iron, the reverse process being found to be equally accurate for the estimation of titanium. Other applications of the new reagent followed, and included methods for the quantitative estimation of certain organic substances, such as the nitro compounds, the azo dyes and dyestuffs, which form colourless leuco compounds when completely reduced. For the estimation of many of these, no quantitative methods had previously existed. Almost the whole of this part of the work was published in three consecutive contributions to the *Berichte der deutschen chemischen Gesellschaft* (1903, 1905, 1907). Some of our work appeared, however, in other journals, and as this was also the case with the work of others on the same subject, it was decided to collate the scattered information and to publish it in the form of a monograph. In Part IV. methods are included for the volumetric estimation of tungsten and molybdenum, in which titanous

chloride does not play any part. As will be seen, the new methods which are based upon the use of titanous chloride already cover a large field in inorganic and organic chemistry, and as they are both rapid and accurate, it is hoped that they will thus be introduced to a larger circle, and will be found useful.

Although a certain amount of practice is required in order to successfully carry out some of the determinations, the methods described are generally such as can be entrusted with confidence to second and third year students, this having been shown to be the case in the laboratories of the Manchester Municipal School of Technology, where they have been in use for some years past.

THE AUTHORS.

TABLE OF CONTENTS

PART I

PREPARATION OF TITANOUS SALTS. TITANOUS SALTS AS QUALITATIVE REDUCING AGENTS

PART II

TITANOUS CHLORIDE AS A QUANTITATIVE REDUCING AGENT

Metals and their Compounds

Non-metallic Elements and their Compounds

Organic Compounds

PART III

Details of Analytical Methods

Non-metallic Elements and their Compounds

PART IV

TUNGSTEN AND MOLYBDENUM

ERRATA

Page 35, line 7 from bottom, *for* " 28·62 %," *read* " 21·62 %."
  ,, 54 ,, 18 ,, ,, *for* " 0·196 grm.," *read* " 1·96 grm."

NEW REDUCTION METHODS IN VOLUMETRIC ANALYSIS

PART I

PREPARATION OF TITANOUS SALTS. TITANOUS SALTS AS QUALITATIVE REDUCING AGENTS

THE reducing agents at present employed in volumetric analysis include ferrous salts, stannous chloride, arsenious oxide, sodium thiosulphate, sodium hydrosulphate, and phenyl hydrazine.[1] Of these only thiosulphate and arsenious oxide are stable in aqueous solution when exposed to the air, and their application is almost entirely restricted to iodimetry. The ferrous salts find their principal application in the standardizing of permanganate, the estimation of chromic acid and its compounds, of chlorates and of nitrates; and stannous chloride finds a limited application in the estimation of ferric iron, and has been used with some success for the estimation of nitro compounds and of some basic dyestuffs. Hydrosulphite of soda has been suggested by Müller as a reagent for the estimation of indigo, while Rawson has used this compound successfully for the estimation of ferric iron.[2] Generally speaking, the methods of volumetric analysis based upon the use of reducing agents are few

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[1] Oxalic acid and sodium oxalate are sometimes employed for standardizing permanganate solutions, but they cannot be regarded as reducing agents in volumetric analysis in any other sense.

[2] *Journ. Soc. Dyers and Col.*, 1885, p. 77.

and far between as compared with acidimetric and alkalimetric, oxidation and precipitation methods. This has been largely due to the want of a sufficiently powerful (energetic) reducing agent which could be maintained at constant strength for a reasonable period.

In 1847, Ebelmen,[1] in describing the reactions of titanous chloride, $TiCl_3$, first drew attention to the strong reducing action of its aqueous solution, and pointed out that it was capable of reducing the salts of copper and iron to their lowest states of oxidation. In the periodic system titanium (with the atomic weight 48) occupies the position in the fourth group intermediate between Silicon (28) and Germanium (72); Tin (118) belongs to the same group, but although its position in the system is considerably lower down (Zirconium intervening), it is the only element of the group of which the salts of the lower oxide (stannous salts) can be compared for practical reasons with the titanous salts.

The element titanium was discovered in 1791 by Gregor in Cornish ilmenite, but it was not until a considerably later period than Berzelius succeeded in isolating the element. It occurs not only widely distributed in nature (as rutile, titanite, ilmenite, etc., and in many clays and bauxites), but also in large quantities. In T. W. Clarke's estimate of the distribution of the elements in the solid earth's crust, oxygen and silicon account for 74·5 % of the total, while titanium is tenth with 0·33 %, and carbon next with 0·22 %.

Titanium forms four distinct oxides, viz.—

TiO, Titanium monoxide or suboxide.
Ti_2O_3,   „   sesquioxide or titanous oxide.
TiO_2,   „   dioxide, titanic acid, or titanic oxide.
TiO_3,   „   peroxide.

[1] *Jahresber.*, 1847–48, p. 402.

The first three of these oxides yield salts with acids, those formed by TiO being blue; but little of a definite character is known of these. Those of Ti_2O_3 are generally violet and in some cases green, those of TiO_2 colourless (except the tannate and gallate, which are of an intense orange colour), while TiO_3 is in itself of an intense orange colour, but yields no definite salts with acids. The oxide TiO_2 is in a sense analogous to SiO_2, inasmuch as when fused with alkalies it yields titanates; but these, unlike the silicates, are instantly decomposed by water. The alkali salts of TiO_3 (pertitanates) are colourless.

Preparation of Titanous Chloride.—The anhydrous salt is obtained by passing a mixture of the vapour of titanic chloride and hydrogen through a red-hot tube. Reduction takes place with simultaneous formation of hydrochloric acid, the titanous chloride being deposited on the cool parts of the tube in the form of scales of a dark violet colour which deliquesce in moist air, forming a reddish-violet liquid.

Aqueous solutions of titanous chloride may be prepared more readily and in several ways, *e.g.* by dissolving the metal in strong hydrochloric acid; by reducing a solution of titanic chloride in hydrochloric acid with different metals, such as zinc, tin, copper,[1] lead, etc. The most suitable of these metals is zinc, either in the form of powder or in the granulated condition. The cheapest and most convenient means of obtaining the aqueous solution is, however, by the electrolytic reduction of a solution of the tetrachloride, or by double decomposition of the electrolytically prepared titanous

---

[1] The reaction with copper seems to be a reversible one, for titanous chloride added to a solution of cupric sulphate will precipitate a portion of the copper as metal.

sulphate [1] with barium chloride. But although the pre-
paration of the salt in the laboratory is not a matter of
any difficulty, the time and trouble involved would pro-
bably deter most chemists from trying the methods de-
tailed in the following pages. For some years past the
product has been made electrolytically on a large scale,
and is placed on the market in the form of a 20 %
aqueous solution at a price which renders it available
for commercial or scientific work. It should be pointed
out that this product contains a small amount of ferrous
chloride, which, however, does not interfere with any of its
applications detailed in the sequel, except for the estima-
tion of chromium, hydrogen peroxide, and persulphates.
Quite recently, however, a solution of pure titanous
chloride has been placed on the market which only
contains traces of iron, and is therefore specially adapted
for analytical work.

By saturating the concentrated aqueous solution with
hydrochloric acid gas, a crystallized salt, having the
composition $TiCl_3 + 6H_2O$ is obtained, in the form of
violet crystals, but experience has shown that in this
form the salt is of little practical utility, on account of
its being too readily oxidized in contact with the air.

Properties and Qualitative Reaction of the Titanous Salts

In dilute aqueous solution titanous chloride exhibits
a beautiful violet colour, but on prolonged exposure to
the air oxidation takes place; [2] the colour gradually fades,

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[1] See N. Evans, *Memoirs of the Manchester Lit. and Phil. Soc.*,
vol. **49**, II. p. 1. Also B. Diethelm, *Inaug. Dissert.*, Zürich, 1908.

[2] The oxidation is not sufficiently rapid to permit of the use of
this reagent for estimating oxygen in gas analysis.

and a precipitate of titanic hydrate forms. The formation of this precipitate may be obviated by the addition of hydrochloric acid in the proportion of one volume of the strong acid to one volume of the commercial solution.

By the cautious addition of an alkali to the solution the colour becomes bluer, while excess of alkali throws down the whole of the titanium as black hydrated titanous oxide (sesquioxide). This immediately begins to decompose the water, and on slightly warming, a brisk evolution of hydrogen takes place—

$$Ti_2O_3 + H_2O = 2TiO_2 + H_2$$
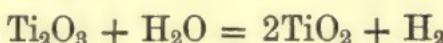
the colour of the precipitate changing from black to white.[1] Exposed to the air, the black precipitate rapidly takes up oxygen and yields titanic hydrate.

The reducing action of titanous chloride is, in the great majority of cases, far more energetic than that of stannous chloride or of other acid reducing agents. With strong nitric acid it reacts violently with evolution of nitrous fumes, a portion of the nitric acid being reduced as far as ammonia. In dilute aqueous solutions strongly acidulated with hydrochloric acid, the reduction of nitric acid takes place, on boiling, to a stage which is intermediate between nitric oxide and nitrous oxide. Chlorates are reduced to chlorides, perchlorates in presence of sulphuric and oxalic acids are likewise reduced to chlorides. Hydrogen peroxide is reduced to water at the ordinary temperature. Salts of persulphuric acid are reduced to sulphates. With sulphurous acid the reaction offers exceptional interest, inasmuch as this acid is reduced instantaneously

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[1] It is remarkable that if the titanous chloride has been formed by the action of tin and hydrochloric acid on titanic chloride, the black precipitate which is obtained by adding excess of caustic soda decomposes very slowly, and can even be boiled, filtered, and dissolved in hydrochloric acid if these operations are conducted rapidly.

to hydrosulphurous acid. Thus, on adding a solution of titanous chloride acidulated with hydrochloric acid to one of sulphurous acid or one of its salts (*e.g.* bisulphite of soda), the violet colour instantly changes to a deep orange-brown, which in a few seconds becomes orange. If excess of caustic soda now be added to the solution and the latter is filtered, the hydrosulphite is found in the filtrate. This constitutes a convenient and rapid laboratory method for the preparation of hydrosulphite of soda for qualitative work. The orange solution alluded to above, which contains the free hydrosulphurous acid is decomposed on standing, but more rapidly on boiling, with deposition of sulphur.

As shown by Ebelmen, ferric salts are reduced to ferrous salts, and it was ascertained that this reduction is quantitative (see below) and takes place in the cold.

Cupric salts are first reduced to cuprous salts, but on adding excess of titanous chloride to a solution of copper sulphate, a portion of the copper is precipitated as metal. Conversely, if titanic chloride is heated with metallic copper, a partial reduction to titanous chloride takes place.

In its action on mercuric chloride, titanous chloride offers a somewhat curious anomaly, for whereas the much weaker stannous chloride instantly precipitates white mercurous chloride, which by excess of the reagent is further reduced to metallic mercury *in the cold*, titanous chloride is without action under these conditions, and only reacts on boiling the solution, when reduction takes place.

Arsenic acid is reduced by titanous chloride in hydrochloric acid solution to arsenious acid, while stannous chloride brings down metallic arsenic under these conditions. In presence of Rochelle salt (sodium-potassium tartrate) and at the boil, titanous chloride gives a copious

brown-black precipitate, which apparently consists of metallic arsenic.

Salts of chromic acid are instantly reduced to chromic salts, and permanganates to manganous salts.

Stannous chloride has apparently no action on titanic chloride, while on the other hand titanous chloride does not appear to react on stannic chloride.

Molybdic and tungstic acids are turned blue by titanous chloride.

The reducing action of titanous chloride on organic compounds is likewise of interest. Of the fatty series, such unsaturated compounds as fumaric and citraconic acids are reduced to the corresponding saturated acids (succinic and pyrotartaric acids). Prussian blue is rapidly decolourized, but the colour of the resulting white compound soon returns to that of the original on exposure to the air. Turnbull's blue behaves similarly.

With potassium ferrocyanide, titanous chloride yields an intensely orange-yellow precipitate, which becomes green on heating.

In the aromatic series a far larger proportion of compounds have been found to give definite reactions with titanous chloride. Thus, the nitro compounds are readily reduced to the corresponding amines. By limiting the amount of reducing agent, it was found possible to reduce one nitro group in m-dinitro benzene, a good yield of m-nitraniline being obtained. Nitrosodimethylaniline is quantitatively reduced at about 40° C. to dimethylphenylene diamine.

Of the oxyazo and amidoazo compounds all that have been tried were completely reduced with consequent permanent decolourization, and there is no reason to suppose that the reaction is not in all cases a quantitative one. A remarkable anomaly was found in the behaviour

of Diamine sky blue and Chrysophenin towards stannous chloride and titanous chloride respectively. The first of these dyestuffs is readily reduced by excess of either reagent, whereas Chrysophenin is only reduced by titanous chloride. If now a mixture of the two dyestuffs is treated with stannous chloride, the blue is discharged, leaving the yellow, as would have been expected. But if the mixture is treated with a limited amount of titanous chloride, the yellow is discharged, leaving the blue. Similar selective reduction, though less pronounced, was also found in other mixtures of azodyes.

Nearly all the dyestuffs which are capable of yielding leuco compounds are reduced by titanous chloride. Thus, finely divided Indigo is reduced first to indigo white, but by the action of a large excess of the reducing agent and at the boil, it is reduced past the condition of indigo white, yielding a yellow substance, which is not reconverted into indigo by oxidation.

Methylene blue,[1] Safranine, and New blue are readily reduced, and are reoxidized by mere contact with the air. The dyestuffs of the triphenylmethane series and their sulphonic acids are reduced in presence of excess of Rochelle salt,[2] and the same applies to the sulphonic acids of Indigotine, Indirubine, Thioindigo red, Rosindone, etc.

---

[1] The reducing action of titanous chloride on Methylene blue may serve as a very delicate test for titanium in qualitative analysis. The solution to be tested is warmed for a few minutes in a test-tube with zinc and hydrochloric acid, and is then added to a very dilute methylene blue solution. If titanium is present decolourization takes place. It is possible in this way to detect titanium in amounts of even less than 0·00001 grm.

[2] According to Piccard (*Berl. Ber.*, 1909, p. 4341), the tartaric acid exerts a catalytic action on the reduction. He recommends the addition of 1 per cent. hydrofluoric acid, which acts similarly.

The Eosines and Rhodamines can be reduced in presence of Rochelle salt and alcohol, whereas all attempts that have hitherto been made to reduce Auramine, Primuline, and Thioflavine have failed. Aniline black is readily reduced by titanous chloride to a dirty brown product. The sulphide colours are likewise reduced, but evidently some change other than mere reduction to the leuco compounds must occur, as they give off considerable quantities of sulphuretted hydrogen.[1] This reaction may be used as a qualitative test for sulphide colours in dyed cotton yarns or fabrics.

Hæmateïn, the colouring matter of logwood, is reduced in presence of Rochelle salt and acetine.

With colouring matters like Indoïne (diazotized Safranine combined with betanaphthol) and Methylene green (Nitro-methylene blue), which contain two chromophores, titanous chloride exerts a selective action as far as the chromophores are concerned. Thus, in reducing Indoine, the azo group is first attacked, and the red colour of the Safranine appears, which on further action is decolourized. In the case of Methylene green, it would appear that the nitro group is first attacked, since by limited action the colour changes from green to the blue colour of amido-methylene blue, and this vanishes on further addition of the reagent.

Quinone is quantitatively reduced by titanous chloride to hydroquinone, while anthraquinone is reduced to dihydro-anthraquinone.

Titanous sulphate, $Ti_2(SO_4)_3$, is obtained by reducing titanic sulphate by means of zinc and sulphuric acid, or

---

[1] For some unaccountable reason, commercial titanous chloride is frequently found to smell of sulphuretted hydrogen. If used as a test for Sulphide colours, it should therefore be boiled with the addition of some hydrochloric acid before use.

by electrolysis. It is more difficult to crystallize than the chloride, but forms double salts with sodium sulphate, which crystallize easily. The salt, having the composition $Ti_2(SO_4)_3 . Na_2SO_4 . 5H_2O$, is readily salted out from its deep purple-black solution at the boil, and crystallizes in cubes of a lilac colour, readily soluble in water. The double salt, $Ti_2(SO_4)_3 . Na_2SO_4 . 12H_2O$, is obtained by spontaneous evaporation of the solution in much larger crystals, which apparently do not belong to the regular system. Commercial titanous sulphate contains 20 per cent. $Ti_2(SO_4)_3$, and is much duller in colour than the chloride. When diluted strongly with water it yields a somewhat turbid solution, the turbidity being caused by the presence of a little titanic sulphate, which dissociates, yielding titanic hydrate.[1]

As a reducing agent, titanous sulphate reacts in most cases like the chloride. In the case of copper sulphate, however, it completely precipitates the copper as metal. The reaction is a very delicate one, and is still visible in solutions containing one part of copper in a million.

[1] The slow decomposition of titanic chloride and sulphate is apt to result in the formation of a white deposit on the containing vessels, which is difficult to remove by the ordinary reagents. Dilute hydrofluoric acid or a boiling solution of potassium binoxalate are the best means for removing this deposit.

PART II

TITANOUS CHLORIDE AS A QUANTITATIVE REDUCING AGENT

METALS AND THEIR COMPOUNDS

IRON AND TITANIUM

IN order to ascertain whether the reduction of ferric salts by titanous salts is quantitative, potassium titanic fluoride which had been recrystallized several times was chosen as standard. An accurately weighed quantity of this salt was reduced in a flask provided with a Bunsen valve, and the cooled solution [1] titrated in a current of carbon dioxide with a solution of ferric chloride of known strength until a sample withdrawn at the end of a glass rod and spotted with potassium sulphocyanide gave a faint red coloration.[2] The following results were obtained :—

K_2TiF_6. Calc. Ti = 18·60 % Found Ti = 18·42, 18·40, 18·56 %
The gravimetric determination gave Ti = 18·47 %.

[1] Instead of being violet, as might have been expected, the solution is green, this colour being probably due to the formation of a double salt of titanous fluoride and potassium fluoride, for titanous fluoride itself is violet.

[2] The spot test was soon afterwards abandoned, as it was found that the direct addition of potassium sulphocyanide to the contents of the flask did not in any way interfere with the delicacy of the reaction, and was much more convenient. It should be noted, however, that a considerable excess of the indicator must be used, as ferric sulphocyanide is decolourized by strong dilution.

Similar results were obtained using recrystallized titanium potassium oxalate, $TiO . C_2O_4 . K_2C_2O_4 . H_2O$ as standard. It is evident, therefore, that the reduction of ferric salts by titanous salts is quantitative, and takes place according to the scheme—

$$TiCl_3 + FeCl_3 = TiCl_4 + FeCl_2$$
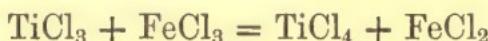
and that we have in this reaction a convenient means for the estimation of ferric iron on the one hand and of titanous and titanic [1] (after reduction) salts on the other. For the volumetric estimation of ferric iron it is claimed that the titanous chloride method, while not ceding anything in point of accuracy to the permanganate method, is considerably more convenient owing to the rapidity with which estimations can be carried out.

Titanium [2] may also be estimated by means of a standard solution of Methylene blue. It is first reduced by zinc and hydrochloric acid to titanous chloride, and the solution is titrated in a current of carbon dioxide with standard Methylene blue (*q.v.*) until a permanent blue colour results. Using titanium potassium fluoride as standard, the following figures were obtained:—

Experiment.	Titanium by methy-lene blue.	By iron.	Gravimetric.
1	18·54 %	18·56 %	18·47 %
2	18·46 ,,	—	—·
3	18·38 ,,	—	—

Theoretical titanium = 18·60 for $K_2TiF_6 . H_2O$

---

[1] See *Berl. Ber.*, 1903, p. 1550. Since the publication of the original paper, G. Gallo, in a communication to the Chemical Society of Rome (Feb. 1907), has described practically the identical process for the estimation of titanium. W. Hinrichsen (*Chem. Ztg.*, 1907, p. 738) has proposed the use of an alloy of zinc and magnesium for the reduction of the titanic salt, and the use of ferric chloride for the subsequent titration.

[2] E. Hibbert, *Jour. Soc. Chem. Ind.*, 1909, p. 189.

Titanium potassium oxalate (dried at 100°) analyzed by the same process gave—

$$14 \cdot 76\% \text{ Ti}$$

Calculated for $TiO . C_2O_4 . K_2C_2O_4$ . . . $15 \cdot 07\%$ Ti

TITANIUM AND IRON IN ADMIXTURE

Since Methylene blue is not reduced by ferrous chloride in hydrochloric acid solution, a titration of the reduced solution containing the two elements only gives the titanium. The iron can be estimated in the unreduced state by direct titration with titanous chloride. To prove that the estimation of the titanium is not affected by the presence of iron, mixtures of known quantities of titanium and iron were prepared, the titanium being estimated by the Methylene-blue method.

Experiment.	Titanium found.	Titanium taken.	Iron taken.
	grm.	grm.	grm.
1	0·03089	0·03094	0·01469
2	0·03867	0·03868	0·03085
3	0·00778	0·00774	0·02938
4	0·00309	0·00309	0·04876
5	0·00158	0·00158	0·04876

When much iron is present, it is necessary to allow the zinc to react for at least twenty minutes in order to ensure complete reduction.

COPPER [1]

By acting on a cupric salt which does not contain oxidizing acids (*e.g.* nitric or chloric acids) with titanous

---

[1] E. L. Rhead, *Trans. Chem. Soc.*, 1906, p. 1491.

chloride, the first effect is to reduce the cupric to the cuprous salt, which separates as a white precipitate. If the titration is done in presence of a known amount of ferric salt and excess of potassium sulphocyanide, selective reduction ensues, the whole of the copper being reduced before the ferric iron is attacked. The end point is reached when the cupric and ferric salts have been reduced to the cuprous and ferrous conditions respectively, so that by subtracting the number of cubic centimetres of titanous chloride required for the known amount of iron present from the total number of cubic centimetres, the difference represents the amount of titanous chloride used for reducing the copper. The reduction may be represented by the following equation :—

$$2CuCl_2 + 2TiCl_3 = 2TiCl_4 + Cu_2Cl_2$$
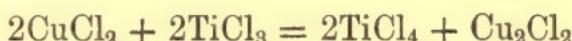
Experiment having shown that cupric salts are readily reduced by ferrous salts in acid solution, and that the amount of titanous chloride used in a copper estimation was the same with or without the addition of pure ferrous salt, the mode of titration was simplified by adding ferrous sulphate and potassium sulphocyanide to the copper solution and titrating direct with titanous chloride.

An amount of copper sulphate corresponding to 0·04988 grm. of copper titrated in this way yielded 0·04986 grm. of the metal.

A sample of electrolytic copper tested by the electrolytic, the potassium iodide, and titanous chloride methods gave the following results :—

Method.	Copper taken.	Copper found.	Percentage.
Electrolytic . . .	0·25 grm.	0·2498 grm.	99·92
Iodimetric . . .	0·25 ,,	0·2497 ,,	99·88
Titanous chloride .	0·25 ,,	0·2496 ,,	99·84

Tin [1]

The main reaction involved in the estimation of this metal is not new, being a reversal of the method worked out by Streng for the estimation of ferric iron by means of stannous chloride. The tin is dissolved in strong hydrochloric acid in a flask (provided with a Bunsen valve) at a temperature below 100° C.,[2] and when solution is complete, the contents of the flask are cooled and a known volume (excess) of standard ferric iron (iron alum) is run in. The contents of the flask are then heated for some minutes on the water-bath, while a current of carbonic acid is maintained through the flask to prevent air oxidation. After cooling, potassium sulphocyanide is added, and the excess of iron alum is estimated by titration with titanous chloride. The method gives good results for metallic tin, and is equally applicable for determining the reducing power of commercial stannous chloride.

The reactions taking place may be represented by the following schematic equations :—

$$Sn + 2HCl = SnCl_2 + H_2\uparrow$$
$$SnCl_2 + 2FeCl_3 = 2FeCl_2 + SnCl_4$$
$$FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4$$
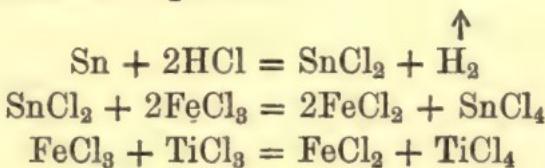
1·1144 grm. of a high-grade commercial pure tin yielded by treatment with nitric acid 1·4146 grm. SnO_2, which calculates out to 99·85 per cent. tin. The same

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[1] *Berl. Ber.*, 1905, p. 3318.

[2] It was ascertained that by *boiling* the tin with hydrochloric acid serious losses may occur in consequence of the fact that stannous chloride is volatile when boiled with strong hydrochloric acid. In one case it was shown that boiling for five minutes occasioned a loss of over 4 per cent. of the total tin present.

sample analyzed in the manner above indicated gave 99·96 and 99·87 per cent. respectively.

The method is also available for the determination of the reducing value of stannous chloride.[1]

CHROMIUM [2]

On chromic salts titanous chloride has apparently no action, but the salts of chromic acid are quantitatively reduced to chromic salts by this reagent. By adding a solution of titanous chloride to a salt of chromic acid containing ferric iron, selective action takes place, the chromic acid being reduced before the ferric iron. No advantage can, however, be taken of this when potassium sulphocyanide is used as indicator, the latter being oxidized by the chromic acid, with the formation of persulphocyanogen. But by adding excess of titanous chloride to the chromic acid solution and then titrating back with standard iron alum in presence of sulphocyanide, the estimation of the chromium can be readily effected.

A sample of pure potassium bichromate titrated by this method gave 99·90 %.

[1] This estimation, which usually constitutes one of the exercises in a course on volumetric analysis, is usually effected by iodimetry. Owing to the fact that stannous chloride rapidly absorbs oxygen from the air, the figures obtained always fall short of the theoretical, and unless the sample has been kept in a hermetically sealed vessel, or has been analyzed immediately before by a competent analyst, no control can be exercised over the result obtained by the student. The analysis of stannous chloride is consequently (unless one of these precautions be taken) about the most unsatisfactory example given to a student in volumetric analysis.

[2] S. B. Jatar, *Journ. Soc. Chem. Ind.*, 1908, p. 673; Hibbert, *ibid.*, 1909, p. 190.

The method is also applicable to chromic salts by converting these into chromates and then titrating as described above. To prove this, a known weight of pure bichromate of potash was reduced to chromic chloride by boiling with strong hydrochloric acid. The chromium was then converted into chromic acid by boiling with sodium peroxide for about ten minutes. Ammonium chloride was then added, and the boiling continued for a few minutes. The solution was then cooled, acidulated with hydrochloric acid, and titrated as indicated above. The amount of chromium found expressed as bichromate of potash was 99·78 %.

For modifications of the method of estimating chromic acid, see Part III., p. 58.

Copper and Chromium in Admixture

In an acidulated solution containing cupric sulphate (or chloride) and a salt of chromic acid, both constituents can be estimated by two separate titrations with titanous chloride. The first titration gives chromium and copper. Another portion of the solution is then treated with sulphurous acid, and, after boiling off the excess of the latter, is titrated again. This gives the copper only. The following results were obtained :—

	Amount taken.	Amount found.
Cr_2O_3	0·02537 grm.	0·02537 grm.
CuO	0·06360 ,,	0·06353 ,,

If, however, the chromium is present as chromic salt, it is not possible to oxidize it quantitatively to the condition of chromic acid by boiling with sodium peroxide, since the copper seems to interfere with the reaction.

The mode of procedure followed in this case was first titrate the copper with titanous chloride in an aliquot part of the solution. In another portion the copper was first removed by sulphuretted hydrogen, the chromium oxidized in the filtrate to chromic acid by boiling with sodium peroxide, with the addition of ammonium chloride, and titrated with titanous chloride. The method was tested with known amounts of copper sulphate and potassium bichromate, the latter being reduced to chromic chloride by boiling with strong hydrochloric acid. The following results were obtained :—

						Amount taken.	Amount found.
Cr_2O_3	.	.	.	.	.	0·02537 grm.	0·02541 grm.
CuO	.	.	.	.	.	0·03180 ,,	0·03185 ,,

COPPER, CHROMIUM, AND IRON IN ADMIXTURE

In a mixture of CuO, Cr_2O_3, and Fe_2O_3, the three metals can be estimated in the following way : The mixture is fused with potassium bisulphate in a porcelain crucible, the melt taken up with water and made up to a known volume.   Aliquot portions of this solution are then treated as follows :—

(1) Iron and copper are titrated together with titanous chloride.

(2) The copper is removed by means of sulphuretted hydrogen, and the iron is determined in the filtrate, after oxidizing with potassium chlorate, by titanous chloride.

(3) After removing the copper with sulphuretted hydrogen, the chromium and iron are oxidized with sodium peroxide, and the chromium and iron estimated together.

The following results were obtained :—

	Amount taken.	Amount found.
Chromium, as Cr_2O_3 . . .	0·02529 grm.	0·02537 grm.
Copper, as CuO	0·03186 ,,	0·03180 ,,
Iron, as Fe_2O_3	0·06197 ,,	0·06197 ,,

NON-METALLIC ELEMENTS AND THEIR COMPOUNDS

HYDROGEN PEROXIDE AND CERTAIN PER-ACIDS

If titanous chloride is added to a solution of hydrogen peroxide, it is instantly oxidized past the condition of TiO_2 to that of TiO_3 (providing always that the hydrogen peroxide is present in excess), and the solution is coloured more or less intensely yellow. By continuing the addition the colour will either increase or decrease in intensity according to the amount of peroxide present, but by continued addition it will disappear altogether, according to the scheme

$$TiO_3 + 2TiCl_3 + 6HCl = 3TiCl_4 + 3H_2O$$

Accordingly, two molecules of titanous chloride (= 2Fe) are required for one of hydrogen peroxide.

The titration is carried out by adding standard titanous chloride solution to a known volume of the hydrogen peroxide under examination until the yellow or orange colour at first formed disappears.

The method was tested against the recognized methods of estimating hydrogen peroxide, using one and the same sample, with the following results :—

By permanganate	10·82 vols. oxygen.
By iodimetry	10·80 ,, ,,
By titanous chloride	10·82 ,, ,,

Perborates may be analyzed in a similar manner. The end point, which consists in the disappearance of the yellow colour, is difficult to perceive in artificial light, and under these circumstances it was found preferable to add titanous chloride in excess and titrate back the excess with iron alum, using potassium sulphocyanide as indicator. The same modification was adopted for the analysis of perborates.[1]   Thus, a sample of sodium perborate yielded the following results:—

	Found.	Calc. for $NaBO_3.4H_2O$.
B_2O_3	22·56 %	22·72 %
Na_2O	20·08 ,,	20·15 ,,
Water of cryst.	46·80 ,,	46·74 ,,
Available oxygen	10·34 ,,	10·39 ,,
	99·78 ,,	100·00 ,,

CHLORATES [2]

Chlorates are readily reduced in the cold by titanous chloride.   Thus, potassium chlorate is quantitatively reduced in a few minutes, according to the equation—

$$KClO_3 + 6TiCl_3 + 6HCl = KCl + 6TiCl_4 + 3H_2O$$
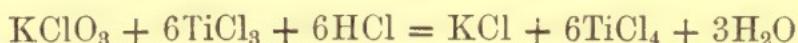
The titration was effected by adding a known amount of the chlorate to an excess of standard titanous chloride solution, allowing to stand for three minutes while a current of carbon dioxide was maintained through the flask, and then titrating back with standard iron alum.

A pure chlorate of potash titrated in this way showed that the reaction is quantitative.   The amount found was 99·78 %.

[1] E. K. Farrar, *Journ. Soc. Dyers and Col.*, 1910, p. 81.

[2] Knecht, *Jour. Soc. Chem. Ind.*, 1908, p. 434.

PERCHLORATES [1]

In dilute aqueous solution the perchlorates are not appreciably reduced by titanous chloride even on prolonged boiling. By a strong solution of titanous sulphate, they are, however, completely reduced, and can be estimated in this way.

The estimation can also be effected by titanous chloride, but only if the latter be used in concentrated solution. The titration of the perchlorate is carried out in fairly strong sulphuric acid solution. The addition of oxalic acid facilitates the reduction in the case of the potassium salt.

The method was tested on chemically pure sodium perchlorate, and the calculation based upon the equation—

$$NaClO_4 + 8TiCl_3 + 8HCl = NaCl + 8TiCl_4 + 4H_2O$$
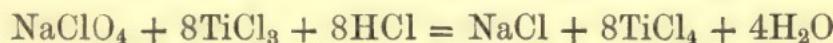
The following result was obtained :—

		Calc. for $NaClO_4 + H_2O$
Perchlorate by titration	86·88 %	87·19 %
Water of cryst.	12·94 „	12·81 „
	99·82 „	100·00 „

NITRATES

For the estimation of nitrates, titanous chloride may be used in several ways.

In the first place, it can be used in Pelouze's process for ascertaining the amount of ferric iron produced from ferrous sulphate by a known amount of nitrate—

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$
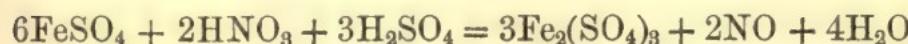
10 c.c. of a 1 % solution of pure potassium nitrate

[1] Rothmund, *Chem. Zeit.*, 1909, p. 1245; Stähler, *ibid.*, p. 759; Knecht and Hibbert, *Proc. Chem. Soc.*, 1909, p. 1.

were boiled with excess of ferrous sulphate free from ferric salt [1] for ten minutes, in a flask through which a current of carbon dioxide was maintained. The solution was cooled, and the ferric iron titrated with titanous chloride.

The analysis gave 99·86 % KNO_3.

The method has a slight advantage over the original one of Pelouze, in that it is not necessary to weigh the ferrous sulphate. The estimation of the ferric iron by titanous chloride is also more convenient than by stannous chloride as recommended by Streng.

Titanous chloride may also serve for the estimation of nitrates (*e.g.* in sewage) by virtue of the fact that in presence of caustic soda titanous hydrate quantitatively reduces nitrates to ammonia. The nitrate to be analyzed is run into a flask (preferably copper) along with excess of caustic soda, and a few cubic centimetres of titanous chloride are added. After swirling and allowing to stand for a few minutes, the ammonia is distilled off into deci-normal sulphuric acid and estimated in the usual way. Pure potassium nitrate titrated in this way gave 99·64 %. Since the titanous chloride contained ammonia, this had to be estimated in a blank experiment and deducted. If the reagent could be obtained absolutely free from ammonia, it would no doubt constitute a very useful means of estimating nitrates in this way.

Small quantities of nitrates in water may also be estimated by heating the concentrate on the water-bath

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[1] The ferrous salt solution used for this estimation is prepared by dissolving ferrous sulphate in water, adding some sulphuric acid, and then a quantity of iron wire. It is not necessary to wait until the whole of the iron is dissolved, but in pouring the solution into the flask in which the reduction is to be effected care must be taken to prevent any particles of metallic iron passing over.

with phenoltrisulphonic acid, and then estimating the picric acid (*q.v.*) formed by titration with titanous chloride.[1]

Pure potassium nitrate titrated in this way gave 99·42 %.

HYDROXYLAMINE

According to Stähler,[2] hydroxylamine is quantitatively reduced to ammonia by the action of titanous salts, according to the scheme—

$$Ti_2O_3 + NH_3O = 2TiO_2 + NH_3$$
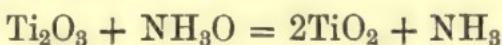
By adding a known amount of hydroxylamine sulphate to excess of titanous chloride and then titrating back the excess of the latter, this author found 99·65 %, and this was in fairly close agreement with the permanganate titration of the same sample (100·15 %).

OXYGEN IN WATER

For the estimation of dissolved oxygen in water, a modification of the Pelouze process was worked out, in which a known volume of the water was mixed with a small amount of ferrous sulphate free from ferric iron. Caustic soda was added in excess, and after shaking and allowing to stand for some time (out of contact with the air) the contents of the flask were acidulated and the ferric iron titrated in the usual way. The results obtained were in very close approximation to those published by Winkler and Pettersen[3] and Roscoe and Lunt,[4] as will be

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[1] F. S. Sinnatt, *Proc. Chem. Soc.*, 1906, p. 255.

[2] *Berl. Ber.*, 1905, p. 4732.

[3] *Berl. Ber.*, 1891, p. 3602.

[4] *Jour. Chem. Soc.*, 1889, p. 552.

seen from the following figures, which show the amounts of oxygen taken up by water from the air expressed in cubic centimetres per litre : —

Temp.				W. & P.	R. & L.	K. & H.
15°	.	.	.	6·94	6·96	6·99
25°	.	.	.	5·69	5·76	5·82

The results obtained by employing manganous hydrate in place of ferrous hydrate were not satisfactory.

HYDROSULPHITES

Although Bernthsen's method of titrating hydro-sulphites in solution (running the hydrosulphite solution into a standard solution of indigo-carmine until the blue colour disappears) leaves nothing to be desired in point of accuracy and of simplicity, the solid hydrosulphite of soda, which is now manufactured and sold in large quantities, is not so easily dealt with. If dissolved in water it begins almost immediately to decompose, with evolution of sulphur dioxide. By dissolving in dilute caustic soda this decomposition can be avoided, but the salt then absorbs oxygen from the air so rapidly that the result of the analysis may be vitiated by an exposure lasting not longer than a few seconds. These difficulties may be overcome by adding a known weight of the hydrosulphite to a known volume (excess) of standard Methylene blue solution contained in a flask through which a current of carbon dioxide is maintained. The hydrosulphite instantly reduces its equivalent of Methylene blue, and that which remains is estimated by titrating with titanous chloride (see under Methylene blue). That the reduction of Methylene blue by hydrosulphite of soda is quantitative was shown by preparing a solution of the hydrosulphite

in weak caustic soda and storing this under hydrogen in an apparatus like that used for titanous chloride (see Part III.). This solution was standardized on pure Indigotine. A titration of the Methylene blue acidulated with acetic acid gave a sharp end point, and the result obtained was exactly the same as that obtained by titration with titanous chloride.

In place of Methylene blue, a standardized solution of indigo extract may be used for the valuation of hydrosulphite of soda. The mode of procedure is the same, and the excess of Indigo may either be determined by titration with standard hydrosulphite or with titanous chloride (see below under Indigo). A solid commercial hydrosulphite of soda gave by titrating the excess of Methylene blue with titanous chloride 87·77 %, and by titrating the excess of Indigo with standard hydrosulphite 87·65 % $Na_2S_2O_4$.

ORGANIC COMPOUNDS

Nitro Compounds

The nitro compounds are quantitatively reduced by titanous chloride in acid solution, and the reduction can be represented, *e.g.* in the case of paranitraniline by the following equation :—

$$C_6H_4 \begin{Bmatrix} NH_2 \\ NO_2 \end{Bmatrix} + 6TiCl_3 + 6HCl = 3H_2O + 6TiCl_4 + C_6H_4 \begin{Bmatrix} NH_2 \\ NH_2 \end{Bmatrix}$$
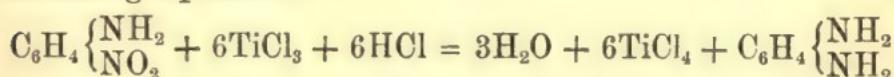
In no case could the disappearance of the colour be taken as the end point of the reaction, as it is not sufficiently sharp. The practice invariably followed was, therefore, to add a known amount of the nitro compound to an excess of titanous chloride, and after boiling for some minutes in a current of carbon dioxide, to cool the

contents of the flask and titrate back the excess of titanous chloride with iron alum, using potassium sulphocyanide as indicator. Nitro compounds which are insoluble in water or in acids (*e.g.* nitrobenzene) may be sulphonated with ordinary or fuming sulphuric acid, while nitro compounds which, like dinitrobenzene, are neither soluble in water nor easy to sulphonate may be dissolved in alcohol and added slowly to the hot solution of titanous chloride contained in a flask through which a current of carbon dioxide is maintained.

The method was shown to give reliable results in the following cases :—

Paranitraniline.—The product crystallized several times from alcohol showed the melting point 147°, and was dried before weighing at 100°. The titration gave—

I. 99·68 %
II. 99·92 „

Sodium Salt of Dinitrostilbene Disulphonic Acid.—The salt recrystallized several times from water and dried at 140° gave 99·82 %.

Nitrobenzene.—This compound, which was chemically pure [1] and showed a melting-point of 7° C., was sulphonated by heating for two hours on the water-bath with twenty times its weight of fuming sulphuric acid (20 % SO_3). The titrations gave the following results :—

I. 99·98 %
II. 99·62 „

Picric Acid.—The volumetric processes for the estimation of this compound include the direct titration with

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[1] We are indebted for this sample to Dr. B. W. Gerland.

caustic soda, using phenol phthalëin as indicator[1] and titration with Night blue on the lines laid down by Ch. Rawson for the titration of Naphthol yellow S.[2] By titration with titanous chloride of a sample recrystallized several times from alcohol and showing a melting-point of 122·5°, the following results were obtained :—

I. 100·13 %
II. 100·16 „

The homologous compounds *sym.* trinitrocressol and *sym.* trinitroxylenol are more difficult to reduce than picric acid, but by using a fair excess of titanous chloride and boiling for about five minutes they are completely reduced.

The molecule of picric acid, containing as it does three nitro groups, requires for its reduction eighteen equivalents of titanous chloride, and it is consequently possible to carry out an exact titration with an amount of picric acid not exceeding one milligramme. This estimation represents, therefore, one of the most accurate in volumetric analysis.

Naphthol Yellow S.—This dyestuff, which was prepared from pure alpha naphthol, has, in the crystallized condition, the composition $C_{10}H_4(OK)(SO_3K)(NO_2)_2 + 1\frac{1}{2}H_2O$.

The analysis gave the following figures :—

	Calculated.	Found.
Colouring matter	93·10 %	93·39 %
Water of crystillization at 140° . .	6·90 „	6·44 „
	100·00 „	99·83 „
Potassium (estimated as sulphate)	20·00 „	19·79 „

m-Dinitrobenzene (m.p. 90°).—This substance is difficult

[1] Kay, *Journ. Soc. Dyers and Col.*, 1888, p. 84.
[2] Knecht, *Ibid.*, p. 83.

to sulphonate even with fuming acid. The method adopted was to dissolve a known weight of the substance in alcohol, and run this solution into a known volume of standard titanous chloride solution (excess) heated to about 80°. The dinitrobenzene at once separates in a fine state of division, and by boiling the contents of the flask for five minutes while passing a current of carbon dioxide, complete reduction was effected. The contents of the flask were then cooled, and the excess of titanous chloride ascertained in the usual way by titration with standard iron alum. The amount of dinitrobenzene obtained in this way was 100·11 %.

Dinitrotoluene (1.2.4., m.p. 71°) analyzed in the same way gave 99·72 %, while dinitronaphthalene (1.8., m.p. 170°) gave 99·74 %.

The method may also serve for estimating the number of nitro groups in an organic compound.

NITROSO COMPOUNDS

Of nitroso compounds, only the technically most important one, viz. *nitrosodimethylaniline*, was tried, and it was found that this was quantitatively reduced at 40–50° according to the equation—

$$C_6H_4 \begin{Bmatrix} NH_2 \\ NO \end{Bmatrix} + 3TiCl_3 + 3HCl = H_2O + 3TiCl_4 + C_6H_4 \begin{Bmatrix} NH_2 \\ NH_2 \end{Bmatrix}$$
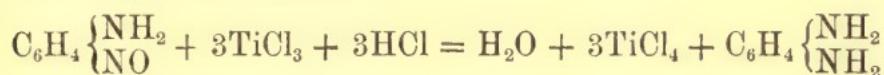
The end point is easily perceived by the disappearance of the yellow colour.

A titration of *nitrosodimethylaniline* which had been purified by recrystallization and showed a melting-point of 85° C. gave 98·88 %.

It was thought that this reaction might be utilized for the valuation of nitrites, and a number of experiments were carried out with this end in view, the principle

adopted being to add slowly a known amount of the nitrite in solution to a cooled solution of dimethylaniline (excess) in hydrochloric acid, and then to titrate the nitroso compound formed. But although satisfactory results were obtained with pure nitrite of soda, it was found that the presence of nitrate (which is the chief impurity) obscured the end point and rendered the method useless for practical purposes.

Azo Compounds

The azo compounds are quantitatively reduced by titanous chloride according to the scheme—

$$R' . N : N . R'' + 4TiCl_3 + 4HCl = 4TiCl_4 + R'NH_2 + R'' . NH_2$$

The method was tested in the first instance on *phenyl azo β naphthol*, $C_6H_5N : N . C_{10}H_6OH$, m.p. 134°. This was sulphonated in the cold with fuming sulphuric acid, and the aqueous solution titrated directly with titanous chloride until decolourized. The titration gave 100·2 %.

Orange II, $C_{16}H_{11}N_2SO_4Na + 5H_2O$, gave the following results :—

	Calculated.	Found.
Colouring matter	79·55 %	79·49 %
Water of crystallization	20·45 ,,	20·42 ,,
	100·00 ,,	99·91 ,,
Sodium (estimated as sulphate) .	5·22 ,,	5·12 ,,

Crystal scarlet 6 *R*, $C_{20}H_{12}N_2S_2O_2Na_2 + 7H_2O$, gave—

	Calculated.	Found.
Colouring matter	79·96 %	80·01 %
Water of crystallization	20 04 ,,	19·96 ,,
	100·00 ,,	99·97 ,,
Sodium (estimated as sulphate) .	7·15 ,,	7·11 ,,

Fast Acid Magenta.—Azo dyestuff prepared by combining diazobenzene chloride with H acid in alkaline

solution, and having the composition $C_{18}H_{11}N_3S_2O_7Na_2 + 6H_2O$.

This dyestuff presents special interest in that when reduced it yields a diamido naphthol disulphonic acid ($OH . NH_2 . SO_3H . SO_3H . NH_2 - 1.2.3.6.8.$), which is turned to an intense red by the addition of iron alum in excess. It can therefore either be titrated directly, the end point being coincident with the disappearance of the colour, or excess of titanous chloride may be added, and standard iron alum then run in until the red oxidation product appears. Both titrations give the same result.

The crystallized dyestuff gave the following results :—

	Calculated.	Found.
Colouring matter	81·92 %	81·6 %
Water of crystallization ($6H_2O$) .	18·08 ,,	17·8 ,,
	100·00 ,,	99·40 ,,
Sodium (estimated as sulphate) . .	7·83 ,,	7·70 ,,

Diamine sky blue (azo dyestuff obtained by combining diazotized dianisidine with H acid in alkaline solution) can be titrated in the same way as the preceding, with this difference, that in using the direct method Rochelle salt should be added.

With *Cotton scarlet*, a dis-azo dyestuff having the composition $C_{22}H_{14}N_4S_2O_7K_2 + 2H_2O$,[1] the amount of titanous chloride required is of course twice as great (calculated on the molecular weight) as for a mono-azo dyestuff. The following results were obtained :—

	Calculated.	Found.
Colouring matter	94·24 %	94·29 %
Water of crystallization	5·76 ,,	5·83 ,,
	100·00 ,,	100·12 ,,
Potassium (estimated as sulphate) .	12·50 ,,	12·57 ,,

[1] The commercial product is the sodium salt.

O. Schmidt having pointed out [1] that azo compounds which contain neither free amido nor hydroxyl groups are not reduced by stannous chloride further than to the condition of hydrazo compounds, it was deemed possible that this might also apply, in some cases at least, to titanous chloride.[2] The p_1-nitro p_2-methoxyazo-benzene used by Schmidt was consequently prepared with a view to ascertaining its behaviour towards titanous chloride.

0·25 grm. was dissolved in 250 c.c. alcohol, and of this 10 c.c. were run into excess of titanous chloride, boiled, cooled, and the excess of titanous chloride titrated back with iron alum. For the complete reduction of the amount of the compound $CH_3O . C_6H_4 . N : N . C_6H_4 . NO_2$ taken, 0·02179 grm. $TiCl_3$ (expressed in terms of Fe) would be required. The amount found by titration was 0·02177.

On the other hand, it was shown by Grandmougin [3] that *o.* nitrophenyl-azo-phenol treated successively by sodium hydrosulphite and stannous chloride was only reduced to the condition of a triazol.

0·1 grm. of this compound was dissolved in 250 c.c. of alcohol, and of this 25 c.c. were titrated as in the previous case. The amount of titanous chloride (expressed in terms of Fe) required for complete reduction is 0·02304 grm., and the amount given by the titration was 0·02304 grm.

With azo dyes like Benzopurpurin 4 B, which are precipitated by acids from their aqueous solutions, the reduction takes place slowly, even at the boil, and this fact makes it difficult to effect a direct titration. But by

[1] *Berl. Ber.*, 1905, p. 3202.

[2] The quantitative estimation of Chrysophenin (*Journ. Soc. Dyers and Col.*, 1905, p. 3) did not support this.

[3] *Berl. Ber.*, 1906, p. 3929.

the addition of an excess of Rochelle salt to the solution, precipitation of the dyestuff is avoided, and a direct titration can be effected in most cases. The following comparisons show that this is the case :—

	Indirect titration.	Direct titration.
Benzopurpurin 4 B	86·80 %	86·50 %
Erika B	82·12 ,,	82·52 ,,

With yellow azo dyes, the end point is not clear in consequence of the formation of the yellowish-coloured titanous tartrate.

For azo dyes like those just referred to, which are precipitated by acids, it is preferable, however, to employ the indirect method, which consists in reducing with an excess of titanous chloride and titrating back with iron alum.

The crystallized potassium salt of Benzopurpurin 4 B, $C_{34}H_{26}N_6S_2O_6K_2 + 4\frac{1}{2}H_2O$ (obtained from diazotized tolidine and naphthionic acid), titrated in this way gave the following results :—

	Calculated.	Found.
Colouring matter	90·33 %	90·26 %
Water of crystallization	9·67 ,,	9·63 ,,
	100·00 ,,	99·86 ,,
Potassium (estimated as sulphate)	9·44 ,,	9·26 ,,

Brilliant Yellow, $C_{26}H_{18}N_4S_2O_8Na_2 + 3H_2O$.—(From diazotized diamidostilbene disulphonic acid and phenol.) The crystallized dyestuff gave the following results :—

	Calculated.	Found.
Colouring matter	92·02 %	91·90 %
Water of crystallization	7·98 ,,	8·00 ,,
	100·00 ,,	99·90 ,,

Chrysophenin,[1] $C_{30}H_{20}N_4O_8S_2K_2 + 6H_2O$.—-Diethylether

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[1] The commercial product consists of the sodium salt.

of Brilliant yellow. The well-crystallized salt gave the following results :—

	Calculated.	Found.
Colouring matter	86·80 %	86·56 %
Water of crystallization	12·20 ,,	13·20 ,,
	100·00 ,,	99·76 ,,

Erika B, $C_{26}H_{19}N_3O_7S_3K_2$.—The crystallized potassium salt gave the following figures :—

Colouring matter	82·12 %
Water at 140°	17·50 ,,
	99·62 ,,

DYESTUFFS WHICH YIELD COLOURLESS LEUCO COMPOUNDS

Under suitable conditions, Indigo (as disulphonic acid) and most of the basic colours (including their sulphonic acids) are quantitatively reduced by titanous chloride, the end point of the reduction being coincident with the disappearance of the colour. The same holds good for the Eosins and rosolic acids.

Methylene Blue, $C_{16}H_{18}N_3SCl$.—This dyestuff is readily decolourized in hydrochloric acid solution by titanous chloride.[1] The direct titration of a sample of pure recrystallized Methylene blue gave the following results :—

Nitrogen found, 12·44 %.   Calculated, 12·57 %.

Colouring matter	95·96 %
Water at 100°	4·00 ,,
	99·96 ,,

The zinc chloride double salt which was obtained in

[1] No Rochelle salt is required for this reduction. If the titanous chloride used contains iron, and Rochelle salt is added previous to the titration, the results will be unreliable, since ferrous salts also reduce Methylene blue in presence of Rochelle salt.

well-defined crystals with a bronze reflex by recrystallization from water, and which has the composition $(C_{16}H_{18}N_3SCl)_2 + ZnCl_2 + H_2O$—

	Calculated.	Found.
Colouring matter	80·53 %	80·38 %

Indigo.—It has already been pointed out (p. 8) that indigotine is reduced by titanous chloride to indigo white. By sulphonating with concentrated sulphuric acid at 90–100°, the indigotine is converted into the water-soluble disulphonic acid, $C_{16}H_8N_2O_2(SO_3H)_2$, and it might have been expected that the aqueous solution of this product would be readily reduced by titanous chloride. Such was, however, not found to be the case, for on adding the reagent to a boiling solution of the dyestuff, the blue colour, though it first rapidly diminished in intensity, changed to a green, which could only be changed to yellow by prolonged boiling with a very large excess of the reducing agent. Many attempts were made to overcome this difficulty, and after numerous failures it was found that the addition of a considerable amount of Rochelle salt gave rise to a perfectly sharp end point,[1] the colour turning from blue to orange.

The test analysis was made with an indigotine which had been crystallized from nitrobenzene and well washed with alcohol. The product contained 0·18 % of ash and 10·51 % nitrogen (calc. for $C_{16}H_{10}N_2O_2$, 10·68 %). This product gave by titration with titanous chloride 99·5 % indigotine.

In another case the indigotine was crystallized from quinoline and gave 99·28 % indigotine.

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[1] When sulphuric acid is present in the solution in large quantity, the addition of Rochelle salt is apt to cause a considerable separation of bitartrate of potash. Sodium tartrate is free from this defect, and can be used with advantage in place of Rochelle salt.

A further sample of indigotine kindly supplied by the Badische Anilin and Soda Fabrik, and stated by them to contain 99·50 % indigotine, was found by our method to contain 99·42 %.

It is thus evident that the reduction of indigotine by titanous chloride is quantitative under the conditions given above. The estimation of indigotine in presence of other substances is dealt with in Part III.

Indirubine.—The estimation of this dyestuff may be effected like that of indigotine, viz. by titrating the sulphonated product in presence of Rochelle salt, and in an atmosphere of carbon dioxide until the red colour disappears.

The indirubine used for the test analysis was a synthetic product kindly supplied by Dr. T. Sandmeyer, which was recrystallized from alcohol and was found to contain 10·47 % nitrogen (calculated for $C_{16}H_{10}N_2O_2$, 10·68 %). The titration gave 99·60 % indirubine.

Thioindigo Red.—For the test analysis the dyestuff was crystallized from benzene, being obtained in this way in the form of large brownish-red leaf-shaped crystals. Solution was effected by warming on the water-bath with fuming sulphuric acid, and the titration was done as with indigo, the end point being very sharp. The substance contained 21·42 % S (calculated for $C_{16}H_8S_2O_2$, 28·62 %), and titrated 100·1 % dyestuff.

TRIPHENYLMETHANE COLOURS

Pararosaniline Hydrochloride.—This was prepared in the laboratory from pure pararosaniline, and was obtained in well-defined crystals. A nitrogen determination gave 10·78 %, whereas the amount required by the formula $C_{19}H_{18}N_3Cl + 4H_2O$ is 10·62 %.

The titration was effected with addition of Rochelle salt, and the following result was obtained :—

	Found.
Dyestuff by titration	81·28 %
Water of crystallization . .	18·60 ,, (calc. 18·28 %)
	99·88 ,,

A known weight of this dyestuff was sulphonated with fuming sulphuric acid, and the trisulphonic acid titrated in the same way as above. The titration gave 81·38 % dyestuff expressed in terms of pararosaniline hydrochloride.

Crystal Violet.—The dyestuff was purified by recrystallization from water. A nitrogen determination gave 7·22 %, whereas the amount required by the formula $C_{25}H_{30}N_3Cl + 9H_2O$ is 7·37 %. The results obtained were as follows :—

Dyestuff by titration	71·67 %
Water of crystallization . .	28·45 ,, (calc. 28·44 %)
	100·12 ,,

Triphenylpararosaniline hydrochloride.—The substance was prepared in the laboratory by phenylating pure pararosaniline, and was purified by recrystallization from alcohol. A nitrogen estimation gave 7·38 % against 7·6 % calculated for $C_{37}H_{30}N_3Cl$. For the titration, which, like the previous titration of rosaniline derivatives, was carried out in presence of Rochelle salt, the product was sulphonated with ordinary sulphuric acid at 100° in order to form the soluble trisulphonic acid. The following results were obtained :—

Colouring matter by titration	93·37 %
Moisture at 120° C.	6·89 ,,
	100·26 ,,

Rhodamine B.—With this dyestuff, as also with the Eosines, it is necessary to add alcohol before titrating. If this addition is omitted, the solution becomes turbid on adding titanous chloride (probably in consequence of separation of the leuco compound), and this obscures the end point. The Rhodamine base used for the test analysis formed well-defined cubical crystals, which transmitted a ruby red light and showed a metallic sheen on the surface. A nitrogen estimation gave 5·16 %, while the nitrogen calculated for the formula $C_{28}H_{31}N_2O_3 + 4H_2O$ is 5·45 %.

For the titration, the base was dissolved in hydrochloric acid, and titrated in presence of Rochelle salt and alcohol. The results were as follows :—

Dyestuff by titration . . . . 86·87 %
Water of crystallization . . . 13·20 ,, (calc. 13·90 %)
————
100·07 ,,

Eosin A.—This dyestuff was obtained in the form of beautiful red needle-shaped crystals by recrystallizing from dilute alcohol. A sodium estimation gave 5·39 %, the amount required for the formula $C_{20}H_6O_5Br_4Na_2 + 10H_2O$ being 5·29 %. The following results were obtained :—

Dyestuff by titration . . . . 79·21 %
Water of crystallization . . . 20·50 ,, (calc. 20·70 %)
————
99·71 ,,

Malachite Green.—The oxalate was used, and this was purified by recrystallization from water. A nitrogen estimation gave 5·85 %, while the formula $2C_{23}H_{24}N_2 + 3C_2H_2O_4 + 2H_2O$ requires 6·04 %.

The following results were obtained :—

Dyestuff by titration . . . . 96·55 %
Water of crystallization . . . 3·40 ,, (calc. 3·60 %)

                                    99·95 ,,

Aurin.—The Aurin prepared from orthocressol and oxalic acid was used, and was obtained in well-defined red crystals by washing the crude product with cold alcohol and then crystallizing from alcohol containing ammonia.

The titration was effected in diluted alcohol in presence of Rochelle salt, and gave 99·5 % of the compound $C_{19}H_{11}O_3 (CH_3)_3$.

The method was also tested on a dyestuff of the *Patent blue* series, having the constitution—
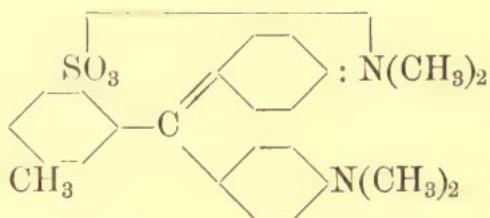
discovered by Dr. T. Sandmeyer.[1] It forms large well-defined dichroic crystals showing a very pronounced metallic sheen. Though not a commercial article, it is of special interest, as it represents the only dyestuff that we have come across which will precipitate tannic acid, but not gallic acid in presence of sodium acetate.[2] Attempts were made to utilize the dyestuff for the quantitative

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[1] *Journ. Soc. Dyers and Col.*, 1896, p. 154.

[2] It is assumed by many that gallic acid is not precipitated by basic colours in presence of sodium acetate or weak ammonia, and methods for the quantitative estimation of tannic acid have been brought forward which are based on this assumption. As a matter of fact, however, all the ordinary basic colours, *e.g.* Magenta, Malachite

estimation of tannic acid by adding excess to a known weight of tannic acid, and titrating the excess of dyestuff in the filtrate. These had, however, to be ultimately relinquished, owing to the sparing solubility of the dyestuff. An analysis gave the following results : nitrogen found, 5·88 % ; calculated for $C_{24}H_{26}N_2SO_3$ (+ 10·8 % H_2O), 5·93 %.

Dyestuff by titration	89·14 %
Water at 100°	10·80 ,,
	99·94 ,,

Of dyestuffs which readily yield leuco compounds, but do not belong to the triphenylmethane series, only three, viz. Safranine, Rosinduline, and Meldola's blue, were tried quantitatively, though it is highly probable that other azines, as well as the oxazines, indamines, and indulines, would give accurate results. On the other hand, Auramine, Thioflavine T, Acridine yellow and Berberine are not reduced by titanous chloride.

Tolusafranine.—The dyestuff used was in the form of large needle-shaped crystals, which were found to contain 13·05 % nitrogen. The formula $C_{21}H_{21}N_4Cl + 3\frac{1}{2}H_2O$ requires 13·09 %.

By titrating in presence of Rochelle salt, the results were invariably 7 to 8 % too high. No satisfactory explanation can be given for this. If, however, bitartrate of soda is used in place of Rochelle salt, the results obtained are almost theoretical—

Dyestuff by titration	86·39 %
Water of crystallization . . .	13·80 ,, (calc. 14·77 %)
	100·19 ,,

green, Safranine, Methylene blue, etc., are quantitatively precipitated by gallic acid in presence of sodium acetate. It is noteworthy that while Methylene blue yields a pure blue tannate, the gallate is violet.

Indoïne.—This dyestuff, which is obtained by combining diazotized safranine with betanaphthol, was obtained for analysis in well-defined crystals. A nitrogen estimation gave 12.28%, while the amount required for the formula $C_{31}H_{26}N_5OCl + 10.30\%$ H_2O is 12.05%. As the dyestuff contains two chromophores, *i.e.* Safranine and one azo group, the amount of titanous chloride required to reduce the molecule is equivalent to 6 of Fe—

Dyestuff by titration 89.42%
Water at 110° . . . . 10.30 „
                                      ———
                                      99.72 „

Rosinduline G.—The colouring matter was purified by recrystallization from dilute alcohol, and after drying at 140°C. was found to contain 6.55% N, while that demanded by the formula $C_{32}H_{13}N_2SO_4Na$ is 6.60%.

The titration was conducted in the usual way, in presence of Rochelle salt, the end point being quite distinct. The following figures were obtained :—

Dyestuff by titration 99.16%
Water at 140° . . . . 0.42 „
                                      ———
                                      99.58 „

Meldola's Blue (New Blue).—This was purified by first extracting the commercial crystallized product with benzene in a Soxhlet, and then recrystallizing from water. In this way the dyestuff is obtained in the form of beautiful long, almost black needle-shaped crystals. A nitrogen determination gave 7.49% N, while that demanded by the formula $C_{18}H_{15}N_2OCl$ is 7.60%.

The titration is done without the addition of Rochelle salt, and it is not necessary to heat the solution. The following figures were obtained :—

Dyestuff by titration . . . . 87·42 %
Water of crystallization . . . 15·27 ,, (calc. for $3H_2O$ 14·51 %)
_____
99·69 ,,

QUINONES

Quinone is reduced by titanous chloride in presence of hydrochloric acid to hydroquinone, the equation

$$C_6H_4O_2 + 2TiCl_3 + 2HCl = C_6H_6O_2 + 2TiCl_4$$

being quantitative. The reaction takes place at the ordinary temperature, and this fact renders the method possible, for if it were necessary to boil, a considerable loss of quinone would ensue owing to its being extremely volatile with aqueous vapour.

The titration may be effected in two different ways. According to the first method, the quinone is dissolved in cold water, a known volume of standard titanous chloride is added, and the excess titrated back with iron alum.

According to the second method, the titration may be done directly by using an indicator. The quinone is dissolved as before in cold water, and a drop of weak Methylene blue solution is added. The solution is now titrated directly with titanous chloride, which exercises a selective action on the two substances in solution, reducing the quinone before attacking the Methylene blue. The end point is therefore reached as soon as the blue colour disappears. In consequence of its great intensity, the amount of Methylene blue required to act as indicator is not sufficient to affect the reading.

The methods were tested on two different samples of pure quinone, one freshly crystallized from water (A), and

the other Kahlbaum's (B) (m.p. 116°), and gave the following results :—

	A.	B.
Method I.	99·84%	99·32 %
Method II.	99·84 ,,	99·32 ,,

Of the two methods we prefer the second as being somewhat shorter, but both methods are accurate.

Toluquinone, $C_7H_7O_2$, prepared by the oxidation of pure freshly distilled orthotoluidine with manganese peroxide and sulphuric acid and showing the m.p. 67°, gave on titrating by Method II. 99·4%.

Orthonaphthoquinone, $C_{10}H_6O_2$, prepared by the oxidation of 1 amido 2 naphthol, was also tried, in order to ascertain whether the process was also applicable to orthoquinones.   The product gave by Method II. 99·70%.

Sugars

The estimation of glucose and other reducing sugars may be rapidly and accurately effected by boiling in the usual way with a known volume of Fehling's solution, and then estimating the copper in the filtrate from the cuprous oxide by means of titanous chloride.   It is of course necessary, in adopting the procedure, to measure the Fehling's solution accurately, and to know exactly the amount of copper that it contains.

The process was tested on a pure recrystallized cane sugar, which was found to contain only traces of ash.   A known weight of this was inverted in the usual way by heating with dilute hydrochloric acid, and was then analyzed as described above.

Assuming that 0·03464 grm. $CuSO_4 . 5H_2O$ is completely reduced by 0·05 grm. dextrose or 0·047 grm. cane sugar, the following results were obtained :—

<div align="center">

I. 100·04 %   II. 100·08 %

</div>

It is, therefore, evident that the presence of the oxidation products of the glucose and levulose had no influence on the accuracy of the copper determinations. It is claimed that the method is more rapid than the usual gravimetric method, while by making up the filtrate from the cuprous oxide to a known volume, and using aliquot parts of this, two or more titrations can be done, thus ensuring greater accuracy.

Colouring Matters in Dyed Cotton Fabrics

Indigo.—The principle of the method is based upon the fact that when indigo-dyed cotton is treated with an 80 % solution of sulphuric acid at about 40° C., the cellulose is rapidly hydrolyzed, passing into solution, while the indigotine is converted into sulphate, $C_{16}H_{10}N_2O_2 . 2H_2SO_4$. On diluting with water, the indigotine sulphate is instantly hydrolyzed with precipitation of indigotine, the products of the cellulose remaining in solution. The indigotine is filtered through a Gooch crucible containing silica or asbestos, washed, dried, sulphonated, and titrated as usual with titanous chloride.

In order to test the method, 7 grms. of cotton yarn and 0·2 grm. of an indigotine of 99·5 % strength were dissolved together in an 80 % solution of sulphuric acid, and the estimation carried out as indicated above. A sharp end point was obtained in the titration, and the amount of indigotine found was 0·1984 grm. in place of 0·1990. The experiment repeated gave 0·1979 grm.

The method was further tested against the acetic acid extraction method of Brylinski (extraction in Soxhlet with glacial acetic acid) on a medium shade of indigo dyed on bleached cloth, with the following results :—

New method . . . . 1·43 % indigotine
Brylinski's method . . . . 1·48 „   „

The only colour commonly used along with Indigo in cotton dying that was found to interfere with the accuracy of the method was manganese bronze, which, if present, may destroy the greater part of the Indigo in the first operation. If found to be present, it can, however, be readily removed by treatment with bisulphite of soda.

Direct Cotton Colours.—The estimation of direct azo dyes in dyed cotton yarns or fabrics can be effected by indirect titration. The mode of procedure is to boil the weighed amount of dyed cotton in dilute hydrochloric acid with an excess of titanous chloride in an atmosphere of carbon dioxide until the colour has been destroyed, and then titrate the excess of titanous chloride with iron alum.

The method was tested by dyeing bleached cotton with a known amount of a direct colour, and estimating separately the amount of colour in the fibre and that left in solution. The following results were obtained :—

<div align="center">

Benzopurpurin 4B.

Amount of dyestuff taken . .	0·10000	grm.
Solution	0·04765	,,
Fibre	0·05230	,,
	0·10000	,,

Chrysophenin.

Amount of dyestuff taken . .	0·05000	grm.
Solution	0·03622	,,
Fibre	0·01399	,,
	0·05021	,,

Erika B.

Amount of dyestuff taken . .	0·05000	grm.
Solution . :	0·03682	,,
Fibre	0·01334	,,
	0·05016	,,

</div>

It was also found possible to estimate in a similar

way a basic colour like Methylene blue dyed on cotton mordanted with tannic acid and tartar emetic. In titrating back with iron alum the end point is marked by the permanent return of the blue.

Amount of dyestuff used . .	0·08450 grm.
Solution	0·00044 „
Fibre	0·08419 „
	0·08463 „

ESTIMATION OF THE DEGREE OF MERCERIZATION IN COTTON YARNS

It is well known that cotton which has been mercerized possesses a greater affinity for colouring matters than before mercerizing, and experience has shown that the amount of a colouring matter like Benzopurpurin 4B which mercerized cotton will take up in dyeing, is in a sense proportional to the strength of the caustic soda which has been used in mercerizing. By dyeing the mercerized cotton along with cotton mercerized with known strengths of caustic soda in one and the same bath with an excess of Benzopurpurin 4B, and then estimating the amount of dyestuff on the fibre in each case, it is possible to arrive at a rough estimate of the strength of caustic soda that has been used in mercerizing the sample in question.

PART III

DETAILS OF ANALYTICAL METHODS

Preparation of the Solution of Titanous Chloride and the Apparatus used for storing it

The solution of titanous chloride for use in the volumetric processes described in this book is prepared in the following way—

50 c.c. commercial titanous chloride (20 per cent. solution) are boiled for about a minute with 100 c.c. concentrated hydrochloric acid in a small flask. The mixture is afterwards cooled and made up to about $2\frac{1}{4}$ litres in the storage bottle A (see Fig. 1). The solution should occupy the entire capacity of the bottle up to the neck, and should be thoroughly mixed by shaking. The lower outlet of the storage bottle is fitted with a rubber stopper, through which a piece of glass tubing is passed. This tubing is bent downwards, and is connected to a bead valve, D^1, which consists of $1\frac{1}{2}$ inches of rubber tubing in the centre of which a pear-shaped piece of glass is inserted. This and a long piece of glass tubing is used to connect the storage bottle to a side opening in the narrow part of the burette below the graduation mark (50 c.c.). The outlet from the burette consists of a bead valve, D^2, similar to that previously described, and a drawn-out glass delivery tube. The stopper in the top of the storage bottle has

two holes. One of these is fitted with a glass tube leading to the top of the burette, and the other has a tube leading to the small hydrogen generator (C). The latter consists of a glass cylinder half filled with a mixture of equal parts hydrochloric acid and water, into which dips an inner tube contracted at the bottom to a narrow aperture, and fitted at the top with a rubber stopper with a hole to receive the tube leading into the storage bottle. This inner tube is filled with ordinary granulated zinc, which is attacked by the hydrochloric acid as soon as the bead valve D^2 is opened. This is done by drawing the rubber tubing from one side of the glass bead by pressure between finger and thumb. The best method of expelling all air from the apparatus is to open the valve D^1, allowing the titanous chloride to flow into the burette and as far as possible up the tube above, then drawing this off entirely by opening the valve D^2 and allowing the hydrogen to escape for some minutes.

Fig. 1.

After this the apparatus is ready for general use.

If any deposit forms on the glass parts of the apparatus, it can be removed, when the storage bottle is refilled, by washing with a one per cent. solution of hydrofluoric acid. The rubber stoppers should be cleaned, from time to
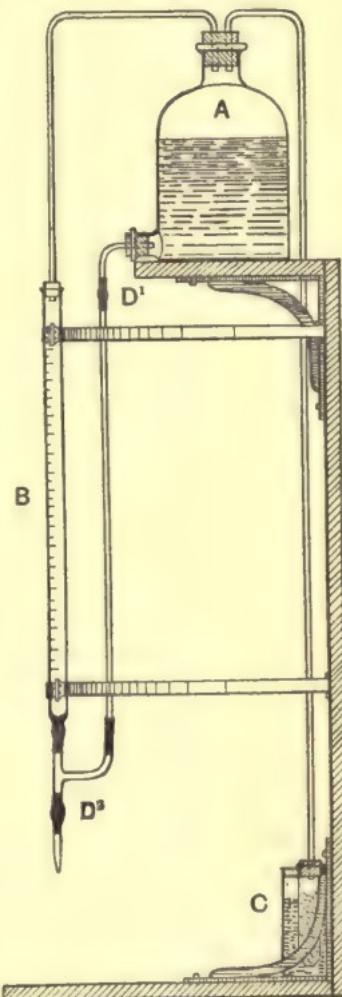
time, by wiping with a cloth soaked in toluene in order to prevent them getting hard.

Standardization of the Solution

The standardization is best effected with the purest ferrous ammonium sulphate. 3·5 grms. of this substance are dissolved in water, and about 100 c.c. 5N sulphuric acid are added. The solution is then made up to 250 c.c. in a graduated flask. 25 c.c. of this solution are carefully oxidized with potassium permanganate of about $\frac{N}{50}$ strength until a faint pink colouration is obtained. A large excess of potassium sulphocyanide is then added, and the ferric iron titrated with titanous chloride until the red colouration due to ferric sulphocyanide entirely disappears.[1] In this connection, it is very important to use a large excess of potassium sulphocyanide as indicator, for the end reaction is thus rendered much sharper. If after oxidation, 25 c.c. of the iron solution require, for example, 26·3 c.c. titanous chloride to reduce it, then 1 c.c. $TiCl_3$ = 0·001901 grm. Fe.

In order to avoid the necessity of oxidizing ferrous ammonium sulphate with permanganate for every standardization, it is best to prepare a large volume (about 10 litres) of iron alum containing about 14 grms. per litre, and acidified with sulphuric acid until the solution assumes a pale straw colour. By measuring the exact

[1] Methylene blue may also be used as indicator in titrating ferric iron, the disappearance of the blue colour only taking place after the whole of the iron has been reduced to the ferrous condition. Since Methylene blue uses up titanous chloride for its decolourization, the amount added should only be such as to just tinge the solution. The end point is perfectly sharp if the solution is warmed previous to titrating to about 35° C.

volume of standard titanous chloride solution required to reduce 25 c.c. of this iron alum solution, using potassium sulphocyanide as indicator, its strength is determined, and as it will retain the same strength for an indefinite period, this iron alum solution may be used in all subsequent cases for standardizing the titanous chloride solution.

ESTIMATION OF METALS

ESTIMATION OF IRON

Ferric Iron.—Solutions of ferric iron may be titrated directly with the titanous chloride solution, using an excess of potassium sulphocyanide as inside indicator. It is immaterial whether the iron is present in sulphuric or hydrochloric acid solution, but the presence of some mineral acid is essential, because the potassium sulphocyanide indicator is otherwise not sensitive.

Ferrous Iron.—This must first be oxidized to the ferric state, and then the estimation is carried out in the manner described above. The method used for oxidizing the ferrous iron to the ferric state may be chosen, according to circumstances, from one of the following:—

1. A known volume of the solution is treated with ammonia and hydrogen peroxide; the excess of oxygen is driven off by boiling for from five to ten minutes, when excess of hydrochloric acid is added sufficient to dissolve the ferric hydrate.

2. To the sulphuric acid solution of ferrous salt add dilute potassium permanganate from a burette until the pink colour just becomes visible.

3. The ferrous solution is treated with a crystal of potassium chlorate and some hydrochloric acid. It is

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then boiled down to a small bulk, some water or hydrochloric acid is added, the solution again evaporated down, and when the excess of chlorine has thus been removed the solution is ready for titration.

Of these processes the first is most generally applicable. Hydrogen peroxide in alkaline solution is easily destroyed, and the ferric hydrate which is formed easily dissolves on acidifying the solution.

The use of potassium permanganate is only possible in the presence of sulphuric acid.

In the third method the excess of oxidizing agent takes a longer time to remove than does the hydrogen peroxide in alkaline solution.

Whichever process of oxidation is selected the subsequent method of estimating the iron is always the same.

EXAMPLES.—1. *Estimation of ferrous and ferric iron in a sample of commercial copperas.* One gram of copperas was dissolved in water and made up to 250 c.c.; 50 c.c. were oxidized with hydrogen peroxide and ammonia as described and then titrated: required 22 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0.001823 \text{ grm. Fe}$$
$$\therefore 50 \text{ c.c. solution contain } 0.001823 \times 22 = 0.040106 \text{ grm. Fe}$$
$$\text{that is, total iron} = 20.05\%$$

Two grams copperas dissolved in water, HCl and potassium sulphocyanide added: required 6·1 c.c. $TiCl_3$.

$$\therefore 2 \text{ grms. copperas contain } 0.001823 \times 6.1 = 0.01112 \text{ grms. Fe}$$
$$\text{that is, } 0.556\% \text{ iron (ferric) or } \frac{0.556 \times 160}{112} = \mathbf{0.79}\% \text{ Fe}_2\text{O}_3$$

The copperas contains, therefore—

$$(20.05 - 0.556) = 19.494\% \text{ iron (ferrous)}$$
$$\text{or } 19.494 \times \tfrac{72}{56} = \mathbf{25.06}\% \text{ FeO}$$
$$\text{corresponding to } \mathbf{96.73}\% \text{ FeSO}_4.7\text{H}_2\text{O}$$

2. *Ferrous and ferric iron in black liquor (ferrous acetate).*—50 c.c. were acidified with HCl and titrated: required 5·4 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0.001756 \text{ grm. Fe}$$
$$\therefore 50 \text{ c.c. contain } 0.001756 \times 5.4 = 0.009482 \text{ grm. Fe}$$
$$\text{that is, } \mathbf{0.1896} \text{ grm. Fe (ferric) per litre}$$

10 c.c. were then made up to 100 c.c., and 10 c.c. of the diluted solution were evaporated to dryness and afterwards ignited, and the residue fused with bisulphate of potash. The product was then dissolved in water, acidified with hydrochloric acid, and titrated with titanous chloride, using potassium sulphocyanide as indicator. This required 31·9 c.c. $TiCl_3$.

10 c.c. of the diluted solution contain, therefore, $0·001756 \times 31·9 = 0·05602$ grms. iron (ferrous and ferric), that is $(56·01 - 0·1896) = \mathbf{55·83}$ grms. iron (ferrous) per litre.

3. *Estimation of ferrous and ferric iron in clay ironstone.*—2 grms. of a finely powdered sample of this ore were dissolved in HCl and the solution made up to 100 c.c.

10 c.c. were treated with ammonia and hydrogen peroxide, boiled, acidified and titrated with titanous chloride, using potassium sulphocyanide as indicator.

29·2 c.c. $TiCl_3$ were required (1 c.c. = 0·002012 grm. Fe).

∴ 10 c.c. or 0·2 grm. contain 0·05875 grm. Fe, and this equals 29·38 % iron (total).

2 grams were dissolved and titrated without previously oxidizing. This required 10·2 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0·002012 \text{ grm. Fe}$$
∴ 2 grms. ore contain $0·002012 \times 10·2 = 0·02052$ grm. Fe
that is, $\mathbf{1·026}$ % iron (ferric)

The sample contains also $29·375 - 1·026 = \mathbf{28·35}$ % iron (ferrous).

4. *Iron in iron wire.*—0·328 grm. iron wire was dissolved in hydrochloric acid, and the solution was made up to 250 c.c. 50 c.c. were treated with ammonia and hydrogen peroxide, boiled to expel excess of oxygen, then acidified and titrated with titanous chloride; 40·55 c.c. $TiCl_3$ were required.

$$1 \text{ c.c. } TiCl_3 = 0·001613 \text{ grm. Fe}$$
∴ 50 c.c. contain $0·001613 \times 40·55 = 0·065407$ grm. Fe
that is, 0·32703 grm. Fe in 250 c.c. = $\mathbf{99·70}$ %

ESTIMATION OF TITANIUM

By reducing a titanic salt with zinc and hydrochloric acid in a flask fitted with a Bunsen valve, the titanium is reduced to the condition of $TiCl_3$, and may be quantitatively estimated by titration with a standard solution

of ferric iron, using potassium sulphocyanide as indicator, or by titration with a standard solution of Methylene blue.

The simple apparatus used for carrying out the reduction of the titanic salt is shown in Fig. 2. It consists of a conical flask (capacity about 200 c.c.), into which the solution of the titanic salt is introduced along with some hydrochloric acid, and is fitted with a rubber stopper having three holes. One hole is fitted with a Bunsen valve, through which a platinum wire having a piece of zinc attached to it is passed, and the other two holes are temporarily closed with two glass rods. In this way the zinc is suspended in the titanium solution, and when reduction has proceeded for 15 to 20 minutes one of the glass rods, A, is removed and a stream of carbon dioxide is passed into the flask, through a tube inserted in the same hole. The zinc is removed from the solution by raising the platinum wire through the small pierced indiarubber stopper at C, and the other glass rod, B, is then removed also. After the zinc has been washed with a little freshly boiled water from a wash-bottle, the solution is cooled and titrated with standard iron alum solution, using potassium sulphocyanide as indicator.
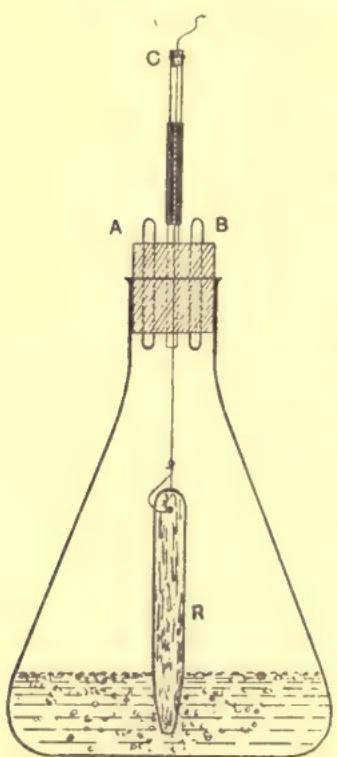
Fig. 2.

As an alternative the titanous solution may be titrated with standard Methylene blue, in which case it is best to boil the solution during the reduction process

with zinc, and to titrate the solution without cooling, in a current of carbon dioxide.

EXAMPLE.—*Determination of titanous and titanic salt in a commercial titanous chloride solution.*

10·24 grms. were taken and diluted to one litre.

25 c.c. of the diluted solution of titanium were reduced with zinc and HCl as described and titrated with iron alum. Iron alum required = 20·3 c.c.

1 c.c. iron alum contains 0·00102 grm. Fe.

$$56 \text{ Fe} = 48 \text{ Ti}$$
$$\therefore 1 \text{ c.c. iron alum} = \frac{0·00102 \times 48}{56} = 0·0008742 \text{ grm. Ti}$$

25 c.c. of the solution contain $0·0008742 \times 20·3 = 0·01775$ grms. Ti. 25 c.c. of the diluted solution were titrated without reducing with zinc: required 19·6 c.c. iron alum.

that is, $0·0008742 \times 19·6 = 0·01713$ grm. Ti (titanous)

The titanium present as titanic salt is $0·01775 - 0·01713 = 0·0062$ grm.; therefore in the original solution there was present—

$$0·01713 \times 40 = 0·685 \text{ grm. Ti (titanous)}$$
$$\text{in } 10·24 \text{ grm.} = \mathbf{21·44} \% \text{ TiCl}_3$$

and $0·71 - 0·685 = 0·025$ grm. Ti (titanic) = **0·96** % $TiCl_4$

TITANIUM AND IRON IN ADMIXTURE

Titanium may be estimated in the presence of iron by reduction with zinc and hydrochloric acid, and titration with either iron alum or Methylene blue, as previously described. Ferrous iron is not oxidized by ferric iron, and consequently the method is useful in the analysis of ores and steel. The amount of iron present is estimated with titanous chloride.

For the determination of titanium and iron in ores, the finely powdered substance is fused with about ten times its weight of caustic potash in a nickel dish. The melt is cooled, treated with water, reduced with zinc and hydrochloric acid in the apparatus described under titanium

and shown in Fig. 2, and then titrated with iron alum or Methylene blue.

The iron is estimated in the dissolved potash melt, which has been acidified with hydrochloric acid by direct titration with titanous chloride, using potassium sulpho-cyanide as indicator.

EXAMPLES.—1. *Estimation of titanium and iron in rutile* (by the iron alum method).

0·4997 grm. of the ore was fused with potash, dissolved in HCl, and made up to 250 c.c.

25 c.c. of this solution were reduced with zinc and hydrochloric acid and titrated with iron alum.

$$\text{Iron alum required} = 17\cdot3 \text{ c.c.}$$

1 c.c. iron alum contains—

$$0\cdot001842 \text{ grm. Fe} = \frac{0\cdot001842 \times 80}{56} = 0\cdot002631 \text{ grm. TiO}_2$$

0·04997 grm. (25 c.c.) contains—

$$0\cdot002631 \times 17\cdot3 = 0\cdot04551 \text{ grm.} = \mathbf{91\cdot07}\% \text{ TiO}_2$$

0·196 grm. ore was fused with potash and dissolved in HCl as above, then titrated with titanous chloride: this required 26·1 c.c. $TiCl_3$.

$$1 \text{ c.c. TiCl}_3 = 0\cdot001432 \text{ grm. Fe} = 0\cdot002046 \text{ grm. Fe}_2O_3$$
$$\therefore 26\cdot1 \text{ c.c.} = 0\cdot05340 \text{ grm. Fe}_2O_3 = \mathbf{2\cdot72}\% \text{ Fe}_2O_3$$

2. *Estimation of titanium and iron in ilmenite* (Methylene blue method).

0·4055 grm. ilmenite fused with potash, dissolved in hydrochloric acid, and made up to 250 c.c.

50 c.c. were reduced with zinc and titrated with Methylene blue solution: required 31·8 c.c.

1 c.c. Methylene blue contains 0·001998 grm. colour.

$$319\cdot5 \text{ Methylene blue solution} = 160 \text{ grms. TiO}_2$$
$$\therefore 1 \text{ c.c. Methylene blue solution} = \frac{0\cdot001998 \times 160}{319\cdot5}$$
$$= 0\cdot0010005 \text{ grm. TiO}_2$$

and 50 c.c. titanium solution contain—

$$0\cdot0010005 \times 31\cdot8 = 0\cdot031816 \text{ grm. TiO}_2 = \mathbf{39\cdot21}\% \text{ TiO}_2$$

50 c.c. of the same solution titrated with titanous chloride required 18·1 c.c.

1 c.c. $TiCl_3$ = 0·001542 grm. Fe = 0·002203 grm. Fe_2O_3

and 50 c.c. solution contain—

$$0·002203 \times 18·1 = 0·039874 \text{ grm. } Fe_2O_3$$

that is, 0·0811 grm. ore contain—

$$0·03987 \text{ grm. } Fe_2O_3 = \textbf{49·16} \% \ Fe_2O_3$$

COPPER

For the estimation of copper in copper sulphate about 1 grm. of the salt is dissolved in water and made up to 500 c.c. 50 c.c. are measured into a conical flask, 10 c.c. standard iron alum solution are added, and 10–20 c.c. of a 10 % solution potassium sulphocyanide. The mixture is titrated with titanous chloride when the copper is first precipitated as white cuprous sulphocyanide, and then the red ferric sulphocyanide is reduced to the colourless ferrous salt, this remaining in solution. The amount of potassium sulphocyanide must be in excess, and as long as this is the case varying amounts of this reagent do not affect the result. The reaction is quantitative in the presence of varying amounts of hydrochloric and sulphuric acid, but nitric acid must not be present. The titration is best carried out at the ordinary temperature or below 30° C., and in an atmosphere of carbon dioxide.

EXAMPLE.—*Copper sulphate.*

A solution was made up containing one gram in 500 c.c.

and 50 c.c. + 10 c.c. iron alum required 26·5 c.c. $TiCl_3$
10 c.c. iron alum required 9·8 c.c. $TiCl_3$
∴ 50 c.c. copper sulphate required 16·7 c.c. $TiCl_3$
1 c.c. $TiCl_3$ = 0·001322 grm. Fe
249·5 grm. $CuSO_4 . 5H_2O$ = 56 grm. Fe

therefore 50 c.c. copper sulphate contain—

$$\frac{0·001322 \times 249·5 \times 16·7}{56} = 0·09833 \text{ grm.} = \textbf{98·33} \%$$

Copper and Iron in Admixture

In mixtures of copper and iron both metals are estimated by the method described for the estimation of copper. Rhead mentions that the copper may be determined separately by removing the iron as acetate and then titrating the copper. The authors have adopted the method of removing the copper as sulphide with sulphuretted hydrogen, and then oxidizing the iron with ammonia and hydrogen peroxide, then boiling off, acidifying, and titrating with titanous chloride according to the method described under Iron.

Example.—0·37 grm. of an ash containing *copper* and *iron* was fused with bisulphate of potash; the fused mass was dissolved in water, made up to 100 c.c., and 25 c.c. were titrated with titanous chloride.

TiCl$_3$ required = 31·0 c.c. (for copper and iron). Another 25 c.c. were taken, sulphuretted hydrogen was passed through the solution, the copper sulphide was filtered off, and the iron in the filtrate was oxidized by boiling with ammonia and hydrogen peroxide. The ferric hydrate was dissolved in HCl and titrated with TiCl$_3$.

TiCl$_3$ required = 16·1 c.c. (for iron); (31·0 − 16·1) = 14·9 c.c. TiCl$_3$ required for copper.

$$1 \text{ c.c. TiCl}_3 = 0.002066 \text{ grm. Fe}$$
$$= 0.002951 \text{ grm. Fe}_2\text{O}_3$$
$$= 0.002914 \text{ grm. CuO}$$

∴ amount of Fe$_2$O$_3$ present in ash = 0·002951 × 16·1 × 4
$$= 0.1900 \text{ grm. Fe}_2\text{O}_3$$
and amount of CuO = 0·002914 × 14·9 × 4
$$= 0.1737 \text{ grm. CuO}$$

The ash contains therefore **51·35** Fe$_2$O$_3$ and **46·95** % CuO

Estimation of Tin

One gram of the metal is dissolved in hydrochloric acid in presence of a small piece of platinum sponge, in a flask fitted with a Bunsen valve. Solution is accelerated by warming on a water-bath, but the temperature must

never be allowed to rise sufficiently high to allow any vapour to escape. When the metal has completely dissolved, the solution is made up to 100 c.c., and 25 c.c. are run into a hot solution of iron alum of known strength, in an atmosphere of CO_2. When the solution has cooled, the excess of ferric iron is titrated with titanous chloride, using potassium sulphocyanide as indicator.

EXAMPLES.—25 c.c. tin solution prepared as described above was allowed to run into 50 c.c. iron alum solution.

(1 c.c. iron alum = 0·005628 grm. Fe.)

It was found that 35·7 c.c. $TiCl_3$ were required to reduce the excess of iron, and this amount corresponded to 7·9 c.c. iron alum.

$\therefore (50 - 7.9) = 42.1$ c.c.

= amount of iron alum required to oxidize $SnCl_2$

112 Fe = 118 Sn
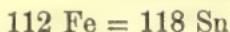
$\therefore$ 42·1 c.c. iron alum oxidize $\dfrac{0.005628 \times 118 \times 42.1}{112} = 0.2495$

and this is contained in 25 c.c. or 0·25 grm. tin = **99·80** %

In this estimation it is necessary to use a more concentrated solution of iron alum than is employed in other cases where titanous chloride is used in volumetric processes, in order that the amount of tin used for the experiment may be large. The method can also be used for estimating the reducing value of stannous chloride.

STANNOUS CHLORIDE

Two grams stannous chloride are dissolved in hydrochloric acid and made up to 100 c.c. with water; 25 c.c. are run into 50 c.c. of a warm solution of iron alum contained in a flask into which carbon dioxide is passed. The solution is allowed to cool, and then the excess of iron is titrated back with titanous chloride, using potassium sulphocyanide as indicator.

EXAMPLE.—25 c.c. of the *stannous chloride* dissolved as described

above were added to 50 c.c. iron alum (1 c.c. = 0·005628 grm. Fe). The amount of titanous chloride required to titrate back was 27·0 c.c. $TiCl_3$ (4·35 c.c. $TiCl_3$ = 1 c.c. iron alum).

Therefore excess iron alum = 6·2 c.c.

$$\text{Iron alum used} = (50 - 6\cdot2) = 43\cdot8 \text{ c.c.}$$

$$\text{The amount of Sn present is } \frac{0\cdot005628 \times 118 \times 43\cdot8}{112} \text{ grms.}$$

$$= 0\cdot2597 \text{ Sn} = \mathbf{51\cdot94}\% \text{ Sn}$$

$$\text{or } \mathbf{99\cdot04}\% \text{ } SnCl_2 \cdot H_2O$$

CHROMIUM

The following methods were suggested by S. B. Jatar.[1]

1. The potassium bichromate is titrated with titanous chloride until a drop taken out of the flask gives no red colouration with a drop of a mixture of pure ferrous sulphate and potassium sulphocyanide solution.

2. The potassium bichromate is allowed to oxidize pure ferrous sulphate, and when all the ferric iron which is formed has been reduced by the titanous chloride, the end of the reaction is indicated by the fact that the solution gives no colouration with potassium sulphocyanide.

The conversion of chromic salts into the condition of chromic acid may be effected by treating with ammonium persulphate in acid solution, and then boiling off the excess of oxygen. We prefer, however, to oxidize with sodium peroxide, boil off the excess of oxygen, and then neutralize with ammonium chloride. This process may be used with advantage for the valuation of chrome alum. It has also been found convenient to titrate the bichromate with excess of titanous chloride, add potassium sulphocyanide, and then titrate back with iron. Whatever mode of procedure is adopted, it is necessary to avoid adding potassium sulphocyanide until all the chromic acid

is destroyed, because chromic acid acts upon ferric sulphocyanide, producing persulphocyanogen.

The following example illustrates the method which was last described :—

EXAMPLE.—Five grams of chromium acetate were dissolved in water and the solution made up to 100 c.c. Of this solution 10 c.c. were treated with sodium peroxide, boiled, the solution neutralized with ammonium chloride, and then titrated with titanous chloride in excess and the excess determined with iron alum.

$$TiCl_3 \text{ used} = 50 \text{ c.c.}$$

Excess by iron alum, 22·4 c.c.; therefore 27·6 c.c. $TiCl_3$ were required by chromium.

$$1 \text{ c.c. } TiCl_3 = 0·001965 \text{ grm. Fe}$$
$$= \frac{0·001965 \times 100}{168} = 0·001169 \text{ grm. } CrO_3$$

$$0·001169 \times 27·6 = 0·0322644 \text{ grm. } CrO_3 \text{ in 10 c.c.}$$

$\therefore$ 50 grms. contain 3·226 grms. $CrO_3 = 6·44 \% CrO_3$

$$= \mathbf{14·75 \%} \text{ chromium acetate}$$

CHROMIUM AND IRON IN ADMIXTURE

The estimation of these metals, in the presence of each other, is best illustrated by an example of the analysis of a sample of chrome iron ore.

The method recommended by Jatar is as follows :—

0·5 grm. of the ore, which has been finely ground and passed through muslin, is fused with caustic soda or a mixture of caustic soda and sodium peroxide, with subsequent additions of the latter, in a silver dish over a Bunsen flame ; after fusing, the mass is extracted with water, the solution is boiled well to remove all traces of hydrogen peroxide, carefully acidified with dilute sulphuric acid, and again boiled.

In this way a mixture of ferric salt and chromic acid is obtained, and the solution may be made up to 500 c.c. and aliquot parts taken for titrations.

50 c.c. of the solution are titrated with titanous

chloride, until all the chromic acid is destroyed, when potassium sulphocyanide is added, and the titration is continued until all the red colour due to ferric sulphocyanide is destroyed. This titration gives the total amount of chromium and iron.

The second titration, which gives the amount of iron alone, is based on the fact that hydrogen peroxide in acid solution reduces chromic acid to the chromic state, while ferric salts remain unchanged. 50–100 c.c. of the solution are taken, and hydrogen peroxide is added: the solution goes purple owing to the formation of chromium peroxide, and afterwards green, showing that the bichromate is reduced to the chromic state. The amount of chromium is obtained by calculation from the difference between the two titrations.

We find that it is possible to estimate the iron alone by other methods. The most rapid method is to boil with hydrochloric acid and a little alcohol, when the bichromate is reduced to chromic chloride. After cooling, the iron, which is not reduced by this treatment, may be titrated directly with titanous chloride.

EXAMPLE.—25 c.c. of a solution containing potassium bichromate and iron alum were found by direct titration to require 30·4 c.c. TiCl₃ = amount required by chromium and iron. 25 c.c. of the solution were boiled with 5 c.c. hydrochloric acid and about 2 c.c. alcohol; the solution was afterwards cooled and titrated as for iron. 25 c.c. treated in this way were found to require

16·2 c.c. TiCl₃ = amount required by iron

30·4 − 16·2 = 14·2 c.c. TiCl₃ = amount required by chromium

1 c.c. TiCl₃ = 0·001742 grm. Fe

168 Fe = 52 Cr

1 c.c. TiCl₃ = 0·000539 grm. Cr

∴ 0·000539 × 14·2 = 0·00765 grm. Cr in 25 c.c. solution

and 0·001742 × 16·2 = 0·02822 grm. Fe in 25 c.c. solution

The solution contains **0·306** grm. Cr per litre

and **1·129** ,,   Fe   ,,

As an alternative, the amount of titanous chloride necessary to reduce both chromium and iron is run into a measured portion of the solution, and the iron may then be titrated back with permanganate, or oxidized with chlorate and hydrochloric acid, which does not attack the chromic salt, but oxidizes the iron to the ferric state ; the latter is titrated with titanous chloride. The last method is one which we have applied in estimating copper chromium and iron present in one solution.

In case iron and chromium are to be estimated in admixture, being present in the form of ferric and chromic oxides, the mode of procedure described in the following example has been found convenient :—

EXAMPLE.—0·228 grm. ash from a piece of cloth was fused with bisulphate of potash, and the fused mass was made up to 100 c.c. with water; 25 c.c. of this solution were titrated with titanous chloride, using potassium sulphocyanide as indicator. $TiCl_3$ required = 16·4 c.c. (for iron). 25 c.c. were oxidized with sodium peroxide as described under chromium. After expelling excess of oxygen, the solution was neutralized and titrated with titanous chloride. $TiCl_3$ required 27·2 c.c. (chromium and iron), so that 27·2 − 16·4 = 10·8 c.c. $TiCl_3$ required by chromium.

$$1 \text{ c.c. } TiCl_3 = 0\cdot001965 \text{ grm. Fe}$$
$$= 0\cdot000889 \quad ,, \quad Cr_2O_3$$
$$= 0\cdot002807 \quad ,, \quad Fe_2O_3$$
$$0\cdot000889 \times 10\cdot8 \times 4 = 0\cdot03840 \text{ grm. } Cr_2O_3$$
$$0\cdot002807 \times 16\cdot4 \times 4 = 0\cdot1841 \quad ,, \quad Fe_2O_3$$
$$Cr_2O_3 = \mathbf{16\cdot84} \%$$
$$Fe_2O_3 = \mathbf{80\cdot97} \%$$

COPPER AND CHROMIUM IN ADMIXTURE

It is necessary in this estimation to have the copper present in the cupric condition, and the chromium as a salt of chromic acid. The amount of titanous chloride required to reduce both copper and chromium is first ascertained, and then alternative methods may be applied

for determining one of the other constituents. The simplest method is to pass SO_2 through the solution, and then, after boiling off excess, titrate the copper with titanous chloride as previously described. Another process, which is somewhat longer, is to first remove the copper with sulphuretted hydrogen, and then to oxidize the chromium to bichromate with hydrogen peroxide, when the bichromate is titrated with titanous chloride in the usual way.

If the copper and chromium are not present in the condition of cupric salt and chromic acid, it is necessary to oxidize and dissolve them. This is the case in determining copper and chromium in the ash of mordanted and dyed material. From 0·2 to 0·3 grm. of the ash is fused with bisulphate of potash; the melt is dissolved in water and made up to a known volume. The copper is first titrated in one portion of the solution, and from another the copper is removed with sulphuretted hydrogen, and the chromium is oxidized with sodium peroxide; the excess of oxidizing agent is removed by boiling, and ammonium chloride is added. The solution is again boiled, then allowed to cool, and is titrated with titanous chloride.

EXAMPLE.—0·279 grm. mixed oxides fused with potassium bisulphate, and made up to 100 c.c.   25 c.c. titrated with $TiCl_3$ for copper estimation required 16·0 c.c.

From 25 c.c. the copper was removed with sulphuretted hydrogen. The chromium was oxidized with sodium peroxide and titrated with titanous chloride : required 26·0 c.c.

$$1 \text{ c.c. } TiCl_3 = 0 \cdot 002001 \text{ grm. Fe}$$
$$= 0 \cdot 002822 \quad ,, \quad CuO$$
$$= 0 \cdot 000905 \quad ,, \quad Cr_2O_3$$

Therefore the ash contains—

$0·002822 \times 16 \times 4 = 0·1806$ grm. CuO = **64·73** %
$0·000905 \times 26 \times 4 = 0·0945$,, Cr_2O_3 = **33·9** %

Copper, Chromium, and Iron in Admixture

These metals are sometimes found together in the ash of mordanted and dyed material, and the following method has been used with success in estimating the mixed oxides. The mixture is fused with potassium bisulphate; the melt is taken up with water and made up to a known volume. Portions of the solution are treated in the following way:—

1. Titrate with titanous chloride, using sulphocyanide as indicator. This gives the amount of iron and copper.

2. The copper is removed with sulphuretted hydrogen, and the iron, after oxidizing with potassium chlorate, is determined by titrating the filtrate with titanous chloride. This gives the amount of iron alone.

3. The copper is removed with sulphuretted hydrogen, and the chromium and iron are oxidized with sodium peroxide. The excess of oxygen is boiled off, hydrochloric acid is added, and the solution again titrated. By this means the total amount of chromium and iron is determined.

EXAMPLE.—The amounts of $TiCl_3$ used in titration were—
  (1) 19·7 c.c. required by iron and copper.
  (2) 8·8 c.c. required by iron.
  (3) 36·2 c.c. required by chromium and iron.

From these figures it will be seen that the copper present required 10·9 c.c., the chromium 27·4, and the iron 8·8 c.c. $TiCl_3$ (1 c.c. $TiCl_3$ = 0·002066 grm. Fe).

$$1 \text{ c.c. } TiCl_3 = 0 \cdot 002951 \text{ grm. } Fe_2O_3$$
$$= 0 \cdot 002914 \text{ ,, } CuO$$
$$= 0 \cdot 000934 \text{ ,, } Cr_2O_3$$

The ash contained, therefore—

$$0 \cdot 002951 \times 8 \cdot 8 \times 4 = 0 \cdot 1039 \text{ grm. } Fe_2O_3$$
$$0 \cdot 002914 \times 10 \cdot 9 \times 4 = 0 \cdot 1270 \text{ ,, } CuO$$
$$0 \cdot 000934 \times 27 \cdot 4 \times 4 = 0 \cdot 1027 \text{ ,, } Cr_2O_3$$

NON-METALLIC ELEMENTS AND THEIR COMPOUNDS

Hydrogen Peroxide

For the analysis of a commercial sample 10 c.c. are diluted with distilled water to 250 c.c. Of this solution, 10 c.c. are titrated with titanous chloride. At first an intense orange-yellow colour appears; this attains a maximum intensity, and then vanishes. The latter point marks the end of the reaction.

EXAMPLE.—10 c.c. hydrogen peroxide (made up as above) required 18·3 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0\cdot002301 \text{ grm. Fe}$$
$$56 \text{ Fe} = 17 \text{ } H_2O_2 = 8 \text{ O}$$
$$\therefore 1 \text{ c.c. } TiCl_3 = \frac{0\cdot002301 \times 8}{56} = 0\cdot0003287 \text{ oxygen}$$

10 c.c. diluted H_2O_2 correspond, therefore, to—

$$0\cdot0003287 \times 18\cdot3 = 0\cdot005025 \text{ oxygen}$$

and 250 c.c. contain—

$0\cdot005015 \times 25 = 0\cdot125$ grm. oxygen
$\therefore$ 10 c.c. strong H_2O_2 contain $0\cdot125$ grm. oxygen
1 grm. oxygen = 697·5 c.c. at 0° C. and 760 mm. pressure

that is, 10 c.c. of the sample evolve 87·47 c.c. oxygen.

$$\text{Hydrogen peroxide} = \textbf{8·75 volumes}$$

Perborates

Perborates can be estimated by the method given for hydrogen peroxide. As an alternative, a known weight of the perborate may be added to an acidulated solution of ferrous ammonium sulphate, and the ferric salt formed titrated with titanous chloride.

EXAMPLE.—0·118 grm. sodium perborate was added to about 2 grms. ferrous ammonium sulphate dissolved in water and acidulated with sulphuric acid. Potassium sulphocyanide was added, and the

solution titrated with titanous chloride, of which 38 c.c. were required.

$$1 \text{ c.c. TiCl}_3 = 0\cdot000323 \text{ grm. oxygen}$$
$$38 \times 0\cdot000323 = 0\cdot01221 \text{ grm. oxygen in } 0\cdot118 \text{ grm. sample}$$
This gives **10·34** % available oxygen

PERSULPHATES

These are estimated indirectly. About 1 grm. of the sample is dissolved in water and the solution made up to 100 c.c. To 10 c.c. of this solution a known volume of titanous chloride is added, the amount being in excess of that required to reduce the persulphate. The excess of $TiCl_3$ is estimated by titrating back with iron alum.

EXAMPLE.—1·02 grm. *ammonium persulphate* was dissolved in water and the solution made up to 100 c.c. To 10 c.c. of this solution 50 c.c. $TiCl_3$ (1 c.c. = 0·002031 grm. Fe) were added. By titrating back with iron alum the excess of $TiCl_3$ was found to be 28·0 c.c., so that 22 c.c. had been used up by the reduction of the persulphate.
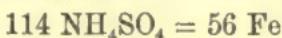
$$114 \text{ NH}_4\text{SO}_4 = 56 \text{ Fe}$$
$\therefore$ 0·102 grm. NH_4SO_4 contain—
$$\frac{0\cdot002031 \times 114 \times 22}{56} = 0\cdot090948 = \mathbf{88\cdot14}\%$$

CHLORATES

These salts are best estimated by introducing a known quantity into an excess of titanous chloride, and titrating back the excess with iron alum. Potassium sulphocyanide is used as the indicator.

EXAMPLE.—*Sodium chlorate.* 0·95 grm. sodium chlorate dissolved in water and made up to 500 c.c.

50 c.c. standard titanous chloride (1 c.c. = 0·0015 grm. Fe) are run into 5 c.c. concentrated hydrochloric acid contained in a conical flask through which a current of carbon dioxide is maintained. 10 c.c. of the sodium chlorate solution are added. After a lapse of not less than three minutes potassium sulphocyanide is added, and the excess

F

of titanous chloride is estimated by titration with standard iron alum solution, until a permanent red colour is obtained. All the values are based upon an iron standard, and six atoms of iron are equal to one molecule of chlorate.

$$106 \cdot 5 \ NaClO_3 = 336 \ Fe$$
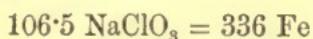
$$1 \ c.c. \ TiCl_3 = 0 \cdot 001513 \ grm. \ Fe = \frac{0 \cdot 001513 \times 106 \cdot 5}{336}$$

$$= 0 \cdot 0004796 \ grm. \ NaClO_3$$

10 c.c. sodium chlorate contain—

$$0 \cdot 0004796 \times 37 \cdot 5 = 0 \cdot 01798 \ grm. \ NaClO_3$$

that is, 0·95 contains 0·899 ;

$$\therefore \ \text{sodium chlorate} = \mathbf{94 \cdot 63} \ \%$$

EXAMPLE.—*Chlorate in bleaching powder.*

The available chlorine was first determined by adding potassium iodide and starch, and titrating with thiosulphate of soda in the presence of acetic acid. This was found to be 31·8 %.

The total chlorine due to hypochlorite and chlorate was estimated in the following way : 10 grms. bleaching powder were made up to 1 litre, and 10 c.c. were titrated with excess of titanous chloride (50 c.c.) in an atmosphere of carbon dioxide, and then titrated back with iron alum.

$$\text{Iron alum required} = 20 \cdot 2 \ c.c.$$

The hypochlorite and chlorate required $50 - 20 \cdot 2 = 29 \cdot 8$

$$1 \ c.c. \ TiCl_3 = 0 \cdot 001162 \ grm. \ Cl$$

$$\therefore \ \text{hypochlorite and chlorate} = 0 \cdot 001162 \times 29 \cdot 8 = 0 \cdot 03463 \ grm. \ Cl$$

$$\text{hypochlorite} = 0 \cdot 03180 \ grm.$$

Therefore the chlorate present corresponds to

$$0 \cdot 03463 - 0 \cdot 03180 = 0 \cdot 00283 \ grm. \ Cl$$

$$= \mathbf{2 \cdot 83} \ \% \ \mathbf{Cl} \ \text{present as chlorate}$$

PERCHLORATES

The estimation of these substances depends upon their complete reduction in concentrated and strongly acid solution. The reduction does not take place in dilute solution. Potassium perchlorate is best dissolved in a strong solution of oxalic acid.

The mode of procedure is best illustrated by the following example :—

EXAMPLE.—Dissolved 0·1125 grm. potassium perchlorate in a saturated solution of oxalic acid, added 10 c.c. concentrated sulphuric acid and 10 c.c. strong titanous chloride (20 %); allowed to stand for about five minutes, then cooled and made up to 100 c.c.

10 c.c. of this solution were titrated with iron alum.

A blank was made with 10 c.c. saturated oxalic acid solution, 10 c.c. concentrated sulphuric acid, 15 c.c. titanous chloride, made up to 100 c.c., and 10 c.c. of this were titrated with iron alum.

iron alum required before adding KClO₄ = 34·8 c.c.
,, ,, ,, after ,, ,, = 21·7 ,,
,, ,, equivalent of TiCl₃ used by KClO₄ = 13·1 ,,

$$1 \text{ c.c. iron alum} = 0 \cdot 002763 \text{ grm. Fe}$$
$$138 \cdot 5 \text{ grm. } KClO_4 = 448 \text{ Fe}$$
$$13 \cdot 1 \text{ c.c. iron alum} = \frac{0 \cdot 002763 \times 13 \cdot 1 \times 138 \cdot 5}{448}$$
$$= 0 \cdot 011182 \text{ grm. in } 0 \cdot 1125 \text{ grm.}$$
$$= \mathbf{99 \cdot 38} \%$$

NITRATES

Two reduction methods are available for the estimation of nitrates.

Method I.—This is really a modification of the Pelouze process, and may be carried out in the following way.

About 1 grm. of the nitrate is dissolved in water and made up to 500 c.c.

About two grams ferrous sulphate (pure) are dissolved in the smallest possible volume of water and 10 c.c. concentrated hydrochloric acid are added. To this there is added 10 c.c. of the nitrate solution. The mixture is boiled in a flask through which carbon dioxide is passed; then allowed to cool and titrated with titanous chloride solution, which estimates the amount of ferric iron produced.

EXAMPLE.—0·996 grm. sodium nitrate was dissolved in 500 c.c.

10 c.c. were allowed to act on ferrous sulphate as above, and the ferric iron titrated with titanous chloride.

$$1 \text{ c.c. TiCl}_3 = 0.001735 \text{ grm. Fe}$$
$$63 \text{ HNO}_3 \text{ or } 85 \text{ NaNO}_3 = 168 \text{ Fe}$$

The solution required 22·1 c.c. TiCl$_3$.

$$1 \text{ c.c. TiCl}_3 = \frac{0.001735 \times 85}{168} = 0.0008777 \text{ grm. NaNO}_3$$

10 c.c. contained—

$$0.0008777 \times 22.1 = 0.019397 \text{ grm. NaNO}_3 = \mathbf{97.8\%}$$

Method II.—This depends upon the nitration of phenol and the estimation of the picric acid formed with titanous chloride.

For this purpose 3 grms. phenol are heated on a water-bath with 20 c.c. conc. sulphuric acid for six hours, and the nitrate to be estimated is heated for an hour on the water-bath with 5 c.c. of this solution. The amount of nitrate taken should correspond to from 0·005 to 0·02 grm. KNO$_3$. The nitro compound is then dissolved in water and titrated with titanous chloride (see Nitro compounds). The mode of procedure is shown in the following example of the estimation of nitrate in water.

EXAMPLE.—*Nitrates in water.* 100 c.c. of the water are evaporated in a porcelain dish, and the residue is treated with 5 c.c. phenol sulphonic acid.

The nitro compound was dissolved in water, hydrochloric acid was added, and the solution titrated with a large excess of titanous chloride (50 c.c.). When this had been cooled, the excess of titanous chloride was titrated back with iron alum, using potassium sulphocyanide as indicator.

$$\text{Iron alum required }[1] = 35.8$$
$$\therefore \text{ TiCl}_3 \text{ used in reduction} = 50 - 35.8 = 14.2 \text{ c.c.}$$
$$1 \text{ c.c. TiCl}_3 = 0.001612 \text{ grm. Fe}$$
$$63 \text{ HNO}_3 = 336 \text{ Fe}$$

---

[1] Here, as elsewhere, it is assumed in these indirect titrations (unless otherwise stated) that the iron alum and titanous chloride solutions are of equal strengths.

and 1 c.c. $TiCl_3 = \dfrac{0.001612 \times 63}{336} = 0.0003022$ grm. HNO_3

100 c.c. water contain $0.0003022 \times 14.2 = 0.00429$ grm. HNO_3

that is, nitrates corresponding to **4.29** grms. HNO_3 in 100,000 c.c. water.

HYDROXYLAMINE

A known amount (about one grm.) of the hydroxylamine salt is dissolved in boiling water, and made up to 100 c.c. An aliquot part of this solution is titrated with excess of titanous chloride in an atmosphere of CO_2.

The excess of titanous chloride is estimated by titrating back with potassium permanganate solution.

EXAMPLE.—1 grm. hydroxylamine hydrochloride, $NH_3O \cdot HCl$, was dissolved in 100 c.c. water, and 10 c.c. were titrated with 50 c.c. $TiCl_3$.

Excess $TiCl_3$ by titrating with permanganate [1] $= 5.9$ c.c. The hydroxylamine required, therefore, 44.1 c.c. $TiCl_3$.

69.5 grms. hydroxylamine hydrochloride $= 112$ Fe

1 c.c. $TiCl_3 = 0.00354$ grm. Fe

$\therefore$ 1 c.c. $TiCl_3 = \dfrac{0.00354 \times 69.5}{112} = 0.002196$ grm.

0.1 grm. hydroxylamine solution contains—

$0.002196 \times 44.1 = 0.09684$ grm. $= $ **96.84** %

OXYGEN IN WATER

The following solutions are required for this estimation :—

10 % solution ferrous sulphate containing a little sulphuric acid and a small coil of iron wire ; 20 % solution of caustic soda ; concentrated hydrochloric acid ; potassium sulphocyanide; and titanous chloride in the storage burette.

Into a flask through which carbon dioxide is passing

[1] In place of permanganate, iron alum can be used for this titration.

100 c.c. of the water to be examined, 5 c.c. ferrous sulphate solution, and 1 c.c. caustic soda are introduced.   The contents are allowed to stand about three minutes, when 1·5 c.c. HCl are added, and 1 c.c. potassium sulphocyanide. The ferric iron is then estimated with titanous chloride.

It is necessary to use small volumes of the reagents, and the capacity of the flask should be about 108 c.c.

EXAMPLE.—A sample of water was treated in the manner described above, and the ferric iron produced was found to require 14·2 c.c. $TiCl_3$.

1 c.c. $TiCl_3$ = 0·0004414 grm. Fe = 0·00006306 grm. O

100 c.c. of the water contain therefore—

$$0·00006306 \times 14·3 = 0·00090176 \text{ grm. O}$$
$$= 6·26 \text{ c.c. oxygen per litre}$$

HYDROSULPHITES

A known weight of the sample is allowed to reduce a solution of Methylene blue.   The latter must be present in excess, and this is estimated by subsequent titration with titanous chloride.

For this purpose a standardized solution of Methylene blue containing about 14 grms. per litre is required. 50 c.c. of this solution are measured into a conical flask, through which a current of carbon dioxide is maintained.

0·1 to 0·2 grm. hydrosulphite is introduced from a weighing bottle, 10 c.c. acetic acid are added; the solution is heated and titrated with titanous chloride.

In order to ascertain how much titanous chloride is required by 50 c.c. Methylene blue solution, this is titrated in the same way, without the introduction of hydrosulphite.

The difference between the number of c.c. $TiCl_3$ required in these two titrations gives the amount equivalent to the hydrosulphite used.

EXAMPLE.—0·1995 grm. *sodium hydrosulphite* was introduced into 50 c.c. Methylene blue, and the solution titrated as described above required 24·4 c.c. TiCl$_3$.

50 c.c. Methylene blue require alone 76·26 c.c. TiCl$_3$.

∴ 76·26 − 24·4 = 51·86 c.c. TiCl$_3$ = 0·1995 grm. hydrosulphite

1 c.c. TiCl$_3$ = 0·002001 grm. Fe

112 Fe = 319·5 Methylene blue = 174 Na$_2$S$_2$O$_4$

∴ 1 c.c. TiCl$_3$ = $\dfrac{0·002001 \times 174}{112}$ = 0·003108 Na$_2$S$_2$O$_4$

58·86 c.c. TiCl$_3$ = 0·003108 × 51·86 = 0·16118 grm. Na$_2$S$_2$O$_4$ corresponding to **80·79** %

Sodium sulphoxylate-formaldehyde (hyraldite, rongalite, hydrosulphite NF).

Sodium sulphoxylate in hydrosulphite NF conc. may be estimated in titanous chloride in a similar way.

EXAMPLE.—A solution of 1·075 grm. in 100 c.c. hydrosulphite NF was employed. 25 c.c. Methylene blue solution (10 grm. per litre) was placed in an Erlenmeyer flask, carbon dioxide was passed in, 10 c.c. acetic acid, and 10 c.c. hydrosulphite NF solution added. The mixture was then allowed to stand 5 minutes, boiled 15 minutes, passing the current of CO_2 into the flask all the time, and then titrated with titanous chloride until the blue colour of the excess Methylene blue was removed.

The hydrosulphite NF reduces its equivalent of Methylene blue, which is expressed in terms of titanous chloride.

25 c.c. Methylene blue required alone 38·13 c.c. TiCl$_3$,

25 c.c. Methylene blue with 10 c.c. hydrosulphite NF required 9·23 c.c. TiCl$_3$;

∴ (38·13 − 9·23) = 28·9 c.c. TiCl$_3$ equivalent to hydrosulphite

1 c.c. TiCl$_3$ = 0·0023 grm. Fe = $\dfrac{0·0023 \times 88}{112}$

= 0·0018 grm. NaHSO$_2$

∴ 10 c.c. or 0·1075 grm. hydrosulphite NF contain 0·0018 × 28·9

= 0·05202

Sodium sulphoxylate = **48·38** %

ORGANIC COMPOUNDS

A. NITRO COMPOUNDS

The indirect method (III.) described for the estimation of azo dyes (see p. 78) is applicable also to all nitro compounds which are soluble in water. Care must be taken, however, to use a large excess of titanous chloride, and to boil for about ten minutes with the reducing agent. By observing these precautions the reduction is complete, six equivalents of titanous chloride being required for the reduction of each nitro group.

EXAMPLE.—*Picric acid*, $C_6H_2(OH)(NO_2)_3$.

1 grm. of picric acid was dissolved in 1 litre of water. 10 c.c. of this solution were acidified with HCl, and 50 c.c. titanous chloride were added; boiled for 10 minutes, and then cooled.

24.1 c.c. iron alum were required to titrate excess $TiCl_3$.

24.1 c.c. iron alum = 26.6 c.c. $TiCl_3$ = excess used

∴ 0.01 grm. picric acid required for reduction 23.4 c.c. $TiCl_3$

229 picric acid = 1008 Fe

1 c.c. $TiCl_3$ = 0.001854 grm. Fe

This amount of the sample contains therefore—

$$\frac{0.001854 \times 229 \times 23.4}{1008} = 0.009856 \text{ grm.}$$

$$= \mathbf{98.56} \%$$

The entire estimation is conducted in a current of carbon dioxide, and this applies to all estimations carried out by the indirect method.

The process has also proved valuable for the estimation of Naphthol yellow S, which requires twelve equivalents of titanous chloride.

Naphthol yellow S, $C_{10}H_4(NO_2)_2 . ONa . SO_3Na$ (disodium salt).

This estimation is conducted in exactly the same way as described for picric acid. An estimation of the disodium salt may serve as an example.

EXAMPLE.—0·25 grm. *Naphthol yellow* was dissolved in 250 c.c. water.

25 c.c. solution required (50 c.c. $TiCl_3$ used ; 27·6 c.c. excess by iron alum) = 22·4 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0.001792 \text{ grm. Fe}$$

358 Naphthol yellow require 672 iron; therefore 25 c.c. solution contain—

$$\frac{0.001792 \times 358 \times 22.4}{672} = 0.02138 \text{ grm. Naphthol yellow S}$$
$$= 85.53\%$$

Trinitrocresol and trinitroxylenol, which also require eighteen equivalents of titanous chloride, and nitrostilbene derivatives such as dinitrostilbene disulphonic acid may also be determined by this method. Paranitraniline is estimated in the same way as picric acid, but the para-nitraniline is first dissolved in hydrochloric acid.

EXAMPLE.—1·013 grm. *p*-nitraniline were dissolved in hydrochloric acid and made up to 1 litre with water. 25 c.c. of this solution were reduced with 50 c.c. $TiCl_3$ in the usual way, and then titrated back with iron alum. Excess $TiCl_3$ = 17·28 c.c.

The *p*-nitraniline uses, therefore, 32·72 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0.001854 \text{ grm. Fe}$$

138 *p*-nitraniline, $C_6H_4NO_2 . NH_2 = 336$ Fe

therefore 0·02532 grm. contains—

$$\frac{0.001854 \times 138 \times 32.72}{336} = 0.02491 \text{ grm.}$$
$$= 98.36\%$$

Compounds like nitrobenzene and nitrotoluene must be sulphonated.

EXAMPLE.—*Nitrobenzene*, $C_6H_5 . NO_2$.

1·002 grms. were sulphonated by heating with 20 c.c. fuming sulphuric acid on a water-bath for 2 hours, and made up to 1 litre.

10 c.c. required $(30 - 14\cdot4) = 15\cdot6$ c.c. $TiCl_3$(1 c.c. $= 0\cdot001745$ grm. Fe)

$$123 \text{ nitrobenzene} = 336 \text{ Fe}$$

therefore $1\cdot002$ contain—

$$\frac{0\cdot001745 \times 123 \times 15\cdot6 \times 100}{336} = 0\cdot9963 = \mathbf{99\cdot43}\%$$

Insoluble nitro compounds which are not easily sulphonated are best estimated by dissolving a known quantity in alcohol, and allowing this to pass into a known volume of titanous chloride acidulated with HCl contained in a conical flask, into which carbon dioxide is passed. The mixture is boiled, then allowed to cool, and the excess of titanous chloride is estimated in the usual way. This method is useful for the valuation of compounds like dinitrobenzene and dinitronaphthalene.

EXAMPLE.—$0\cdot1002$ grm. *dinitronaphthalene*, $C_{10}H_6(NO_2)_2$ $1\cdot8$, was dissolved in 250 c.c. alcohol.

50 c.c. $TiCl_3$ were measured into a conical flask, hydrochloric acid was added, CO_2 passed over, and 25 c.c. of the dinitronaphthalene solution run in. The mixture was boiled, then allowed to cool, and afterwards titrated back. Iron alum required $= 31\cdot55$ c.c. $TiCl_3$.

Therefore the dinitronaphthalene solution required $18\cdot45$; but 25 c.c. alcohol alone required $0\cdot8$ c.c., so the dinitronaphthalene used $17\cdot65$ c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0\cdot001742 \text{ grm. Fe}$$
$$218 \text{ dinitronaphthalene} = 672 \text{ Fe}$$

therefore $0\cdot01002$ grm. taken contains—

$$0\cdot009974 \text{ grm.} = \mathbf{99\cdot54}\%$$

NITROSO COMPOUNDS

The nitroso compounds can be titrated directly in hydrochloric acid solution. About 1 grm. of the nitroso compound is dissolved in hydrochloric acid and made up to 250 c.c. 50 c.c. of this solution are warmed over a Bunsen to about 40–50° C., CO_2 is passed into the flask,

and the solution is then titrated with titanous chloride until the intense yellow colour is completely destroyed. Four equivalents of titanous chloride are required for the reduction of each nitroso group.

EXAMPLE.—*p. Nitrosodimethylaniline*, $C_6H_4N(CH_3)_2NO$. 50 c.c. solution prepared as above required 20·15 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0.001476 \text{ grm. Fe}$$
$$150 \text{ nitrosodimethylaniline} = 224 \text{ Fe}$$

therefore 50 c.c. solution contain—

$$\frac{0.001476 \times 150 \times 20.15}{224} = 0.19914 \text{ grm.} = \mathbf{99.52} \%$$

NAPHTHALENE IN COAL GAS

The method depends upon the formation of naphthalene picrate and the estimation of the picric acid by means of titanous chloride, and only differs from the process described for the estimation of picric acid in that the naphthalene picrate is dissolved in alcohol.

Naphthalene picrate is separated by any of the usual processes, and about 20 c.c. alcohol and 20 c.c. concentrated hydrochloric acid are added. The solution is boiled, excess of titanous chloride is added, and after cooling, the excess of titanous chloride is estimated by means of iron alum, using potassium sulphocyanide as indicator.

EXAMPLE.—Naphthalene picrate, obtained by passing a litre of coal gas through a solution of picric acid, was dissolved in alcohol and reduced as described above with 50 c.c. $TiCl_3$

$$\text{Excess } TiCl_3 = 30 \text{ c.c. (by iron alum)}$$
titanous chloride used by picric = 20 c.c.
$$1 \text{ c.c. } TiCl_3 = 0.001784 \text{ grm. Fe}$$
$$1008 \text{ Fe} = 229 \text{ picric} = 126.98 \text{ naphthalene}$$
$$\therefore 1 \text{ c.c. } TiCl_3 = 0.0002248 \text{ grm. naphthalene}$$
The amount present = 0·004496 grm. naphthalene per litre

B. The Estimation of Azo Dyes

Method I.—Azo dyes, which are not precipitated by dilute hydrochloric acid, may be titrated directly. This applies to colours like Orange II., Orange G, Scarlet 2G, Crystal scarlet 6R, Scarlet R, Fast red, etc. The azo group requires four equivalents of titanous chloride.

EXAMPLES.—1. *Crystal scarlet.* 0·5 grm. dyestuff was dissolved in distilled water and made up to 500 c.c. 100 c.c. were measured into a conical flask, and after adding 10 c.c. concentrated hydrochloric acid, was boiled for about a minute and then titrated with titanous chloride, of which 17 c.c. were required.

$$1 \text{ c.c. TiCl}_3 = 0.001712 \text{ grm. Fe}$$
$$502 \text{ C}_{20}\text{H}_{12}\text{N}_2\text{O}_7\text{S}_2\text{Na}_2 = 224 \text{ Fe}$$
$$\therefore \frac{0.001712 \times 17.1 \times 502}{224} = 0.06559 \text{ grm. colour}$$

and 1 grm. contains—

$$0.6559 \text{ Crystal scarlet} = \mathbf{65.59}\%$$

2. *Scarlet* 2G. 0·5 grm. dissolved in 500 c.c.

100 c.c. solution required 23·1 c.c. TiCl$_3$(1 c.c. TiCl$_3$ = 0·001876 grm. Fe)
$$452 \text{ grm. Scarlet 2G} = 224 \text{ grm. Fe}$$

therefore 100 c.c. solution contain—

$$0.08743 \text{ grm.} = \mathbf{87.43}\%$$

Orange II.—1 grm. was dissolved in 500 c.c. water. 50 c.c. required 31·7 c.c. TiCl$_3$.

$$1 \text{ c.c. TiCl}_3 = 0.001554 \text{ grm. Fe}$$
$$350 \text{ C}_{16}\text{H}_{11}\text{N}_2\text{O}_4\text{SNa} = 224 \text{ Fe}$$

therefore 50 c.c. solution contain—

$$\frac{0.001554 \times 350 \times 31.7}{224} \text{grm.} = 0.07681 \text{ grm.}$$
$$= \mathbf{76.81}\%$$

This estimation of azo dyes affords a ready method of determining the maximum quantity of any of these colours which is absorbed in dyeing wool. The amount of colour taken up by wool which has been dyed with

50 % Orange G, for example, is ascertained in the manner described below, and this serves to illustrate the mode of procedure.

One gram of wool was dyed for 1 hour with exactly 50 % of Orange G and 30 % sulphuric acid. After the dyeing process was complete, and the wool had been removed from the bath, the latter was made up to 500 c.c., and 50 c.c. were titrated with titanous chloride (1 c.c. $TiCl_3$ = 0·001418 grm. Fe); 50 c.c. colour required 11·8 c.c. $TiCl_3$

$$452 \ C_{16}H_{10}N_2S_2O_7Na_2 = 224 \ Fe$$

that is, $\dfrac{0·001418 \times 452 \times 11·8}{224} = 0·03376$ grm. Orange G

500 c.c. contain therefore 0·3376 grm. Orange G, and the wool has taken up 0·5 − 0·3376 = 0·1624 grm. = **16·24 %**

Method II.—Many of the azo dyes which are precipitated by hydrochloric acid can be titrated directly in the presence of Rochelle salt.

A known weight of the dyestuff is dissolved in water, and a definite volume of the solution, together with a solution of Rochelle salt, is titrated with titanous chloride.

The process has been found useful in the valuation of Diamine black, Diamine violet, Benzo green, etc., and we have used it successfully for pure Benzopurpurin and Erika, but commercial samples of these two dyestuffs do not always give distinct end reactions, and the indirect method (III.) of titrating azo dyes is to be preferred for their exact valuation.

EXAMPLE.—1 grm. *Diamine black B.H.* was dissolved in water and made up to 250 c.c. 50 c.c. colour solution with 25 c.c. Rochelle salt (20 %) required 18·9 c.c. $TiCl_3$.

$$1 \ c.c. \ TiCl_3 = 0·001742 \ grm. \ Fe$$
$$960 \ C_{34}H_{24}O_{14}N_6S_4Na_4 = 448 \ Fe$$

The solution contains therefore—

$$\frac{0·001742 \times 960 \times 18·9 \times 5}{448} = 0·3518 \ grm.$$
$$= \textbf{35·18 \%}$$

Method III.—The direct cotton yellows like Chryso-phenine cannot be estimated with titanous chloride by direct titration, because acids precipitate them, and Rochelle salt forms a compound with titanium which in dilute solution is pale yellow, and interferes with the end reaction in the titration of yellow colours by Method II. An indirect method is therefore applied. A known amount of colour solution is boiled in a conical flask into which carbon dioxide is passed, hydrochloric acid is added, and an excess of titanous chloride is run into the mixture. The contents of the flask are again boiled until the colour has been destroyed, which will usually take place in about two minutes, and the flask then cooled in an atmosphere of carbon dioxide which is maintained through the flask throughout the estimation. When cold the excess of titanous chloride is estimated by titrating with standard iron alum solution with potassium sulphocyanide solution as indicator. By subtracting the number of c.c. of the iron alum solution (or their equivalent in titanous chloride, should the two solutions not be of equal strength) from the total number of c.c. of titanous chloride run in, the exact amount of the reducing agent used up by the dyestuff is arrived at.

EXAMPLES.—1. *Chrysophenine G.* ($C_{30}H_{26}N_4O_8S_2Na_2$). 1 grm. of the colour was dissolved in water and made up to 1 litre; 100 c.c. were boiled, hydrochloric acid was added, and 50 c.c. of titanous chloride. The mixture was boiled until all the precipitate dissolved and the solution acquired a slight violet tint, due to the excess of $TiCl_3$. It was then cooled by allowing a stream of water to circulate round the flask, and it was then titrated back with iron alum.

$$1 \text{ c.c. } TiCl_3 = 0.001712 \text{ grm. Fe}$$
$$1 \text{ c.c. iron alum solution} = 1.03 \text{ c.c. } TiCl_3$$
$$680 \text{ Chrysophenine} = 448 \text{ Fe}$$
$$100 \text{ c.c. Chrysophenine} + 50 \text{ c.c. } TiCl_3 \text{ required } 25.2 \text{ c.c. iron alum.}$$
$$25.2 \text{ iron alum} = 26.0 \text{ c.c. } TiCl_3$$
$$\therefore \text{ amount of } TiCl_3 \text{ used by Chrysophenine} = 24 \text{ c.c.}$$

therefore 0·1 grm. or 100 c.c. Chrysophenine solution contain—

$$\frac{0\cdot001712 \times 680 \times 24}{448} = 0\cdot06235 \text{ grm.}$$
$$= \mathbf{42\cdot35}\%$$

2. *Benzopurpurin 4B.*—1·005 grm. dissolved in 500 c.c. 100 c.c. reduced with titanous chloride 50 c.c.

$$1 \text{ c.c. } TiCl_3 = 0\cdot001845 \text{ grm. Fe}$$
$$724 \text{ } C_{34}H_{26}N_6S_2O_6Na_2 = 448 \text{ Fe}$$
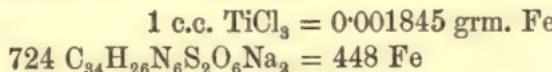
required 30·2 c.c. iron alum (1 c.c. = 0·99 c.c. $TiCl_3$) = 29·9 c.c. excess $TiCl_3$ and 20·1 c.c. $TiCl_3$ used by Benzopurpurin.

$$\therefore 50 \text{ c.c. or } 0\cdot1005 \text{ grm.} = \frac{0\cdot001845 \times 724 \times 20\cdot1}{448} = 0\cdot05981 \text{ grm.}$$
$$= \mathbf{59\cdot81}\%$$

DIAMINE SKY BLUE AND AZO COMPOUNDS WITH H. ACID

Titanous chloride decolourizes a solution of Diamine sky blue, but on exposure to air or when iron alum is added the colourless solution assumes a red colour. This is characteristic of the colouring matters prepared by combining diazo compounds with H. Acid.

It is possible to estimate such colours as Fast acid magenta, Diamine sky blue, etc., by boiling in an atmosphere of carbon dioxide, titrating with excess of titanous chloride, and then titrating back with iron alum until a faint red colour appears. For evidence of the quantitative reaction, see p. 30.

EXAMPLE.—0·942 grm. *Diamine sky blue* was dissolved in water and made up to 250 c.c.

25 c.c. were titrated with 20 c.c. $TiCl_3$.

$$\text{Excess of } TiCl_3 \text{ by iron alum} = 7\cdot6 \text{ c.c.}$$

therefore 12·4 c.c. $TiCl_3$ were required by colour.

$$992 \text{ } C_{34}H_{24}N_6O_{16}S_4Na_4 = 448 \text{ Fe}$$
$$1 \text{ c.c. } TiCl_3 = 0\cdot001542 \text{ grm. Fe} = 0\cdot003422 \text{ grm. colour}$$
$$\therefore 25 \text{ c.c. contain } 0\cdot003422 \times 12\cdot4 = 04243 \text{ grm. colour}$$
$$\text{or } \mathbf{44\cdot43}\%$$

Although the direct titration (Method I. for azo dyes) applies to colours of the same type as Fast acid magenta, and direct titration (Method II.) with Rochelle salt or sodium tartrate applies to Diamine sky blue, the indirect method described above is important as it is the method adopted in estimating Diamine sky blue on dyed cotton fabrics.

C. *DYESTUFFS YIELDING COLOURLESS LEUCO COMPOUNDS*

METHYLENE BLUE

One gram is dissolved in 250 c.c. water; 50 c.c. are measured into a conical flask, a small quantity of hydrochloric acid is added, carbon dioxide is passed into the flask in the manner described for Indigo, and the contents are heated over a Bunsen flame. Titanous chloride is then run in until the blue colour just disappears.

$$C_{16}H_{18}N_3SCl + H_2 = C_{16}H_{20}N_3SCl$$
$$319 \cdot 5 \text{ Methylene blue} = 112 \text{ iron}$$
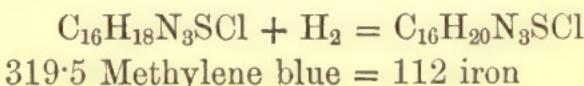
EXAMPLE.—0·97 grm. *Methylene blue* was made up to 250 c.c. 50 c.c. of this solution required 32·4 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0 \cdot 001563 \text{ grm. Fe}$$
$$= 0 \cdot 004458 \quad ,, \quad \text{Methylene blue}$$

therefore 50 c.c. or 0·194 grm. Methylene blue contains—

$$0 \cdot 1444 \text{ grm. } C_{16}H_{18}N_5SCl = \textbf{74·45} \%$$

INDIGO

Pure Indigo can be estimated by titrating the sulphonated dyestuff with titanous chloride in the presence of Rochelle salt or sodium tartrate and in an atmosphere of carbon dioxide.

For this purpose 1 grm. of the sample is mixed with 5 c.c. pure sulphuric acid, and heated in a water-oven at 95° C. for one hour. The contents of the vessel are then cooled, and are dissolved in water and made up to 500 c.c. 50 c.c. of this solution and 50 c.c. of Rochelle salt or sodium tartrate (20 % solution) are introduced into a conical flask fitted with a rubber stopper having three
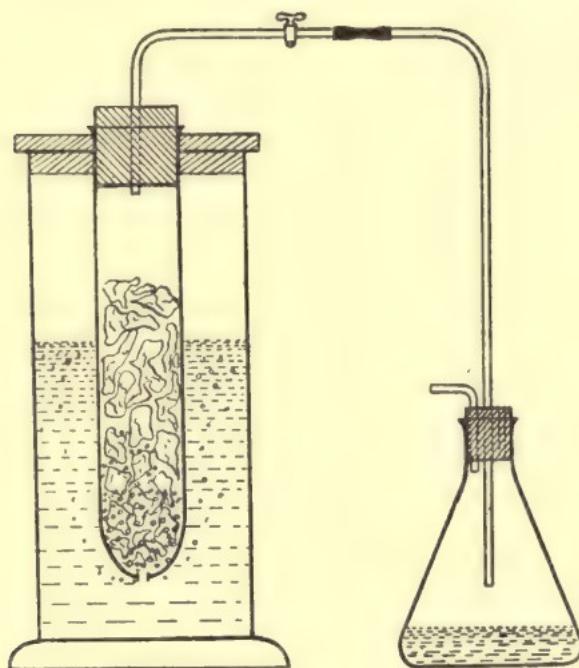
Fig. 3.

holes. Through one of them a current of carbon dioxide is introduced, another is fitted with a tube for the escape of the gas, and a third is left for the delivery tube of the titanous chloride burette (see Fig. 3). The solution is boiled and then titrated with titanous chloride. In this process the indigo is reduced to indigo white, and the solution assumes a yellow colour when the reaction is complete.

G

EXAMPLE.—50 c.c. Indigo solution prepared as above required when titrated in presence of sodium tartrate 21·30 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0·0020 \text{ grm. Fe}$$
$$262 \ C_{15}H_{10}N_2O_2 = 112 \text{ Fe}$$
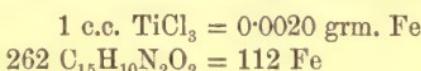
50 c.c. solution contain therefore—

$$0·09964 \text{ Indigo} = \textbf{99·64} \% \text{ indigotine}$$

Commercial Indigo usually contains impurities which are liable to interfere with the end reaction in this titration, and several processes have been devised by means of which the indigotine may either be isolated or freed from impurities, and in that condition it is possible to estimate the Indigo by titration with $TiCl_3$.

These purification processes include—

1. Grossmann's modification.

One gram of Indigo is treated with 5 c.c. H_2SO_4 (100 %) at 95° C. for one hour. The sulphonic acid is cooled, dissolved in about 400 c.c. water, and pure calcium carbonate is added until the solution is neutral; it is then made up to a convenient volume (*e.g.* 1 litre) and allowed to settle. An aliquot part is then decanted off and titrated with $TiCl_3$ as described for pure Indigo.

EXAMPLE.—100 c.c. indigo solution prepared as above required 12·8 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0·001695 \text{ grm. Fe}$$

therefore 100 c.c. contain—

$$\frac{0·001695 \times 262}{112} = 0·05075 \text{ Indigotine}$$
$$= \textbf{50·75} \%$$

2. Bloxam's method depends upon the production and isolation of indigotine tetrasulphonate of potash in the following way :—

One gram of Indigo is sulphonated by heating on a water-bath with 5 c.c. of 20 % fuming sulphuric acid for half an hour. The product is then poured into water and

made up to 500 c.c. 100 c.c. are transferred to a large beaker, and 100 c.c. of a solution of potassium acetate (450 grms. per litre) added. The mixture is boiled, then cooled first in a stream of water and then with ice for one hour. Indigotine tetrasulphonate of potash separates out, and this is filtered off through a Gooch crucible. It is then washed with a solution prepared by adding 5 c.c. glacial acetic acid to 200 c.c. of the potassium acetate solution and 400 c.c. water, until the washings lose their brown colour and assume a pale blue tint. The tetrasulphonate is then dissolved in boiling water and titrated with titanous chloride in the manner described for pure indigo.

Example.—Indigotine tetrasulphonate from 0·2 grm. indigo was dissolved in 100 c.c. water. 50 c.c. solution required 16·2 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0\cdot001172 \text{ grm. Fe}$$

50 c.c. contain therefore—

$$\frac{0\cdot001712 \times 262 \times 16\cdot2}{112} = 0\cdot06558$$
$$= \mathbf{65\cdot58\,\%}$$

3. Möhlau and Zimmermann's process.

0·1 grm. of Indigo is heated with 100 c.c. glacial acetic acid and 5 c.c. concentrated sulphuric acid for 20 mins. on a water-bath, and the solution poured into water and filtered. The precipitate consists of finely divided crystallized indigotine, which can be filtered through a Gooch, sulphonated and titrated with titanous chloride.

The results obtained by this method are slightly high as compared with other processes.

Example.—0·1 grm. required 18·2 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0\cdot001645 \text{ grm. Fe}$$

0·1 grm. Indigo contain therefore—

$$\frac{0\cdot001645 \times 262 \times 18\cdot2}{112} = 0\cdot07003$$
$$= \mathbf{70\cdot03\,\%}$$

The error to which this method is liable has been pointed out by Grossmann and also by Bergtheil.

4. Purification with 80 % sulphuric acid.

This method is based upon the following facts :—

(*a*) Indigo is soluble in 80 % sulphuric acid, forming a sulphate which when poured into water dissociates with separation of indigotin as such. This sulphate, according to Binz and Kufferath,[1] has the composition $C_{16}H_{10}N_2O_2 . 2H_2SO_4$.

(*b*) That other products which may be present as impurities in Indigo are either soluble in 80 % sulphuric, but remain in solution on the addition of water, or they do not yield to the subsequent sulphonation process.

This process, which has proved to be a convenient one, is carried out in the following way :—

0·2 grm. Indigo is treated with about 10 c.c. of 80 % sulphuric acid for a quarter of an hour with frequent stirring, and the temperature is maintained at about 40° C. 100 c.c. water are then added, and after boiling, the Indigo is filtered through a Gooch crucible. The filtering medium may be either sand and asbestos or preferably a filter bed about $\frac{1}{3}''$ deep, consisting of a layer of coarsely crushed quartz, then finer quartz, and as the upper layer a little finely divided silica.

The precipitate is washed, dried, and sulphonated with ordinary sulphuric acid in the usual way. It is then dissolved in water and titrated with titanous chloride in the presence of sodium tartrate and in an atmosphere of carbon dioxide.

EXAMPLES.—1. *Artificial Indigo.*

$$1 \text{ c.c. TiCl}_3 = 0.001982 \text{ grm. Fe}$$

0·2 grm. Indigo required 40·1 c.c. $TiCl_3$;

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[1] *Lieb. Ann.*, 1903, 325.

therefore 0·2 grm. contains—

$$\frac{0 \cdot 001982 \times 262 \times 40 \cdot 1}{112} = 0 \cdot 1859 \text{ grm.}$$

$$= \mathbf{92 \cdot 95} \%$$

2. *Artificial Indigo paste.*

1 c.c. $TiCl_3 = 0 \cdot 001864$ grm. Fe

0·2 grm. Indigo required 12·1 c.c. $TiCl_3$; therefore 0·2 grm. contains—

$$\frac{0 \cdot 001884 \times 12 \cdot 1 \times 262}{112} = 0 \cdot 04199 \text{ grm.}$$

$$= \mathbf{20 \cdot 99} \%$$

3. *Natural Indigo.*

1 c.c. $TiCl_3 = 0 \cdot 002013$ grm. Fe

0·2 grm. Indigo required 20·1 c.c. $TiCl_3$; therefore 0·2 grm. contains—

$$\frac{0 \cdot 002013 \times 20 \cdot 1 \times 262}{112} = 0 \cdot 09465 \text{ grm.}$$

$$= \mathbf{47 \cdot 33} \%$$

MAGENTA

One gram of this dyestuff is dissolved in 500 c.c. water. 50 c.c. of this solution and 25 c.c. of a 20 per cent. Rochelle salt solution (or sodium tartrate) are boiled and then titrated in a current of carbon dioxide.

EXAMPLE.—0·969 grm. *Magenta* was dissolved in water and made up to 500 c.c. 50 c.c. of this solution required 15·5 c.c. $TiCl_3$.

1 c.c. $TiCl_3 = 0 \cdot 001724$ grm. Fe

323·5 $C_{19}H_{18}N_3Cl = 112$ Fe

∴ 1 c.c. $TiCl_3 = 0 \cdot 004979$ grm. p. rosaniline hydrochloride

0·0969 grm. contains 0·007717 grm. $C_{19}H_{18}N_3Cl$

= **79·64** % *calculated as p. rosaniline hydrochloride*

83·06 % *calculated as rosaniline hydrochloride,* $C_{20}H_{20}N_3Cl$

ACID MAGENTA

The commercial product is the sodium salt of the trisulphonic acid of magenta. It is titrated in exactly the same way as magenta.

EXAMPLE.—1 grm. *Acid Magenta* was dissolved in water and made up to 100 c.c. 50 c.c. solution required 24·1 c.c. TiCl$_3$.

$$611 \ C_{19}H_{16}N_3O_{10}S_3Na_3 = 112 \ Fe$$
$$\text{or } 625 \ C_{20}H_{18}N_3O_{10}S_3Na_3 = 112 \ Fe$$
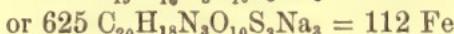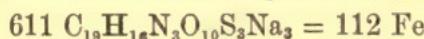
1 c.c. TiCl$_3$ = 0·001821 grm. Fe = 0·01194 $C_{20}H_{18}N_3O_{10}S_3Na_3$

50 c.c. colour contain 0·01016 × 24·1 = 0·2448

trisulphonic acid of rosaniline = **48·96** %
or *trisulphonic acid of pararosaniline* = **47·88** %

EOSIN A

When Eosin is treated with titanous chloride in the presence of Rochelle salt decolourization ensues, but the solution becomes turbid owing probably to the separation of the leuco compound. In consequence of this the end reaction is indistinct. By adding an equal volume of alcohol to the solution before titrating a definite end reaction is obtained, and the solution becomes yellow on reduction.

EXAMPLE.—1·04 grm. *Eosin A* was dissolved in water and the solution made up to 250 c.c. 50 c.c. of this solution were mixed with 25 c.c. Rochelle salt solution (20 %) and 50 c.c. alcohol. Carbon dioxide was passed over the solution, which was then boiled and titrated with titanous chloride.

1 c.c. TiCl$_3$ = 0·001672 grm. Fe

50 c.c. Eosin solution required 10·2 c.c. TiCl$_3$.
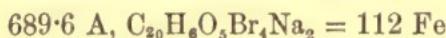
$$689·6 \ A, \ C_{20}H_6O_5Br_4Na_2 = 112 \ Fe$$
1 c.c. TiCl$_3$ = 0·010294 grm. Eosin

50 c.c. or 0·20 grm. Eosin solution contains 0·1049 grm.
= **50·46** %

RHODAMINE

This colour is estimated in the same way as Eosin.

EXAMPLE.—1·01 grm. Rhodamine B was dissolved in water and made up to 250 c.c. 50 c.c. colour solution, 25 c.c. Rochelle salt, and 50 c.c. alcohol were boiled in an atmosphere of carbon dioxide,

and titrated with titanous chloride; required 10·6 c.c. (1 c.c. $TiCl_3$ = 0·001901 grm. Fe).

$$478·5\ C_{28}H_{31}N_2O_3Cl = 112\ Fe$$
$$\therefore 1\ \text{c.c. } TiCl_3 = 0·008121\ \text{grm. Rhodamine}$$

50 c.c. or 0·202 grm. contains 0·08609 grm. Rhodamine
$$= \mathbf{42·61\ \%}$$

MALACHITE GREEN

The titration of this dyestuff is carried out in exactly the same manner as described for Magenta. This product behaves in a somewhat different manner towards the reducing agent, however. After the addition of 3 to 4 c.c. of the titanous chloride solution the colour disappears momentarily, returns again, and then disappears in the same way with the next addition. The colour reappears, however, and it is only when the reaction is complete that the colour no longer reappears.

EXAMPLE.—1·12 grm. *Malachite green* were dissolved and made up to 250 c.c. with water; 50 c.c. were taken, along with 25 c.c. Rochelle salt, and were found to require 23 c.c. $TiCl_3$.
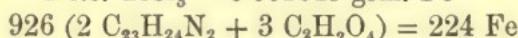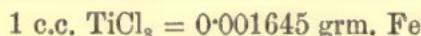
$$1\ \text{c.c. } TiCl_3 = 0·001645\ \text{grm. Fe}$$
$$926\ (2\ C_{23}H_{24}N_2 + 3\ C_2H_2O_4) = 224\ Fe$$
$$\therefore 1\ \text{c.c. } TiCl_3 = 0·00680\ \text{grm. Malachite green}$$

50 c.c. solution or 0·224 grm. contains 0·1564 grm. Malachite green
$$= \mathbf{69·82\ \%}$$

ANILINE BLUE

Pure triphenyl pararosaniline is prepared by heating pararosaniline with freshly distilled aniline and a little benzoic acid. The melt is treated with excess of hydrochloric acid, and the hydrochloride is then filtered off, washed with water, and recrystallized from alcohol.

The product obtained in this way has the formula

corresponding to triphenyl pararosaniline, and may be estimated in the following way :—

The product is first sulphonated for an hour with concentrated sulphuric acid at 100° C. made up to a known volume with water, and then an aliquot part of this is mixed with Rochelle salt or sodium tartrate, and is titrated in an atmosphere of carbon dioxide with titanous chloride.

EXAMPLE.—0·495 grm. *Triphenyl pararosaniline* was sulphonated with 5 c.c. conc. H_2SO_4 and made up to 250 c.c. with water; 50 c.c. of this solution required 10·7 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0.001869 \text{ grm. Fe}$$
$$551.5 \ C_{37}H_{30}N_3Cl = 112 \text{ Fe}$$
∴ 50 c.c. or 0·099 grm. sample contains 0·09847 grm. $C_{37}H_{30}N_3Cl$
$$= \textbf{99·46} \%$$

The Aniline blue of commerce consists mainly of diphenylrosaniline and di- and tri-phenylpararosaniline.

SAFRANINE

The results of our experiments point to the fact that the reduction of Safranine in alkaline solution is not normal, and as the amount of Rochelle required for the titration of colours brings about this condition, it has been found necessary to use sodium bitartrate instead of Rochelle salt in the estimation. In other respects the estimation of this dyestuff resembles the process described for Magenta.

EXAMPLE.—1 grm. of *Tolusafranine* was dissolved in 250 c.c. water; 50 c.c. were measured into a conical flask, 25 c.c. of a saturated solution of sodium bitartrate were added, the mixture was boiled and titrated with titanous chloride in an atmosphere of carbon dioxide.

50 c.c. safranine solution required 24·2 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0.001642 \text{ grm. Fe}$$
$$364.5 \ C_{21}H_2N_4Cl = 112 \text{ Fe}$$

50 c.c. or 0·2 grm. contain 0·1293 grm. Safranine = **64·65** %

INDOÏNE

This dyestuff, which is prepared by combining diazo-tized Safranine with β naphthol, is first reduced by titanous chloride to Safranine, and the latter is then further reduced to the leuco compound. The mode of procedure is exactly the same for the analysis of Indoïne as that described for Safranine. The azo group requires four and the Safranine two equivalents of hydrogen for reduction, making a total of six, or 6 Fe.

EXAMPLE.—0·5 grm. *Indoïne* dissolved in 500 c.c. ; 50 c.c. required with bitartrate of soda 18·1 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0·001529 \text{ grm. Fe}$$
$$519·5 \ C_{31}H_{26}N_5OCl = 336 \text{ iron}$$
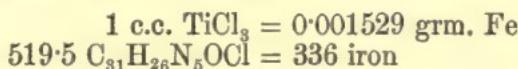
therefore 50 c.c. contain—

$$\frac{0·001529 \times 519·5 \times 18·1}{336} = 0·4287 \text{ grm.}$$
$$= \mathbf{85·56} \% \text{ indoïne}$$

QUINONES

A number of quinones may be estimated by direct titration with titanous chloride, using Methylene blue as indicator.

Benzo and toluquinones are dissolved in cold water, naphthoquinone is dissolved in alcohol or glacial acetic acid, but the former is to be preferred as a solvent for this purpose. About 0·25 to 0·1 grm. of substance is used for the estimation, and a suitable strength of Methylene blue to be used as indicator is 0·5 grm. per litre. One drop of this is added to the solution of quinone to be estimated, the titanous chloride not destroying the blue colour until all the quinone has been reduced.

EXAMPLE.—*Benzoquinone.* 0·0998 grm. was dissolved in water and made up to 100 c.c.; 25 c.c. of the solution required 17·6 c.c. $TiCl_3$.

$$108 \ C_6H_4O_2 = 112 \ Fe$$
$$1 \ c.c. \ TiCl_3 = 0·001408 \ grm. \ Fe$$
$$= 0·001357 \ grm. \ quinone$$

therefore 25 c.c. solution contain—

$$0·001357 \times 17·6 = 0·02388 \ grm. \ in \ 0·0499 \ grm. \ sample$$
$$= \textbf{95·71} \ \% \ quinone$$

D. *ESTIMATION OF SUGARS*

I. GLUCOSE

For this estimation, Fehling's solution prepared in the following way is required.

34·64 grms. $CuSO_4 . 5H_2O$ are dissolved in water and made up to 500 c.c.

51·6 grms. caustic soda and 173 grms. Rochelle salt are dissolved, mixed, and made up to 500 c.c.

Equal volumes of each of these solutions are used in the estimations. 100 c.c. of this solution are equivalent to 0·7787 grm. Fe.

50 c.c. of a 1 % solution of the sugar are added to 100 c.c. of Fehling's solution, and the mixture is boiled for two minutes; 100 c.c. of cold water are then added, and the cuprous oxide is filtered off. The filtrate is acidified and made up to a known volume (500 c.c.). An aliquot part (25 c.c.) is titrated with titanous chloride, and in that way the amount of copper remaining in the filtrate is ascertained. (This process is carried out in the manner described for the estimation of copper, see p. 55.) The amount of copper reduced by the glucose is found by difference, and from this the amount of glucose is calculated from the factor. 0·3464 grm. $CuSO_4 . 5H_2O$ is completely

reduced by 0·05 grm. glucose, or since one of iron is equivalent to one of copper sulphate, 1 grm. Fe = 0·6416 grm. glucose.

EXAMPLE.—*Estimation of glucose.* Amount of glucose taken, 1·051 grm. This was dissolved and made up to 100 c.c.; 50 c.c. glucose solution were treated with 100 c.c. Fehling's solution as described. The cuprous oxide was filtered off, and the filtrate was made up to 500 c.c.; 100 c.c. of this solution were titrated with titanous chloride in order to estimate the copper precipitated. The solution required 16·2 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0·002013 \text{ grm. Fe}$$
$$16·2 \text{ c.c. } TiCl_3 = 16·2 \times 0·002013 = 0·03261 \text{ grm. Fe in } 100 \text{ c.c.}$$
$$\text{or } 0·16305 \text{ in } 500 \text{ c.c.}$$

The extent of the reduction is therefore

$$0·7787 - 0·1630 = 0·6157 \text{ grm. Fe}$$
$$\text{and since } 1 \text{ grm. Fe} = 0·6416 \text{ grm. glucose}$$
$$0·6157 \text{ grm. Fe} = 0·6157 \times 0·6416 = 0·3950 \text{ grm. glucose in } 50 \text{ c.c.}$$
$$\text{or } 0·79 \text{ grm. glucose in } 100 \text{ c.c.}$$
$$1·05 \text{ contains } 0·79 = \mathbf{75·23 \%}$$

II. CANE SUGAR

This must first be inverted, and the process is best carried out in the following manner:—

50 c.c. of a 10 % solution of sugar are measured into a 500 c.c. flask, and 5 c.c. pure hydrochloric acid are added.

The flask is warmed on a water-bath to 65° C. with frequent shaking for ten minutes. The subsequent procedure is the same as in the estimation of glucose.

0·3464 grm. $CuSO.5H_2O$ is completely reduced by 0·0475 grm. cane sugar, or 1 grm. Fe = 0·6097 grm. cane sugar after inversion.

EXAMPLE.—3·764 grms. *sugar* dissolved and inverted as described were made up to 500 c.c.; 50 c.c. treated with 100 c.c. Fehling's

solution and filtered; filtrate made up to 500 c.c.   50 c.c. of this
solution required 8·4 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0.002032 \text{ grm. Fe}$$
$$8.4 \text{ c.c. } TiCl_3 = 8.3 \times 0.002032 = 0.01708 \text{ grm. Fe in 50 c.c.}$$
$$\text{or } 0.1708 \text{ in 500 c.c.}$$

The extent of the reduction is therefore

$$0.7787 - 0.1708 = 0.6079 \text{ grm. Fe}$$
and since 1 grm. Fe = 0·6097 grm. cane sugar (inverted)
$$0.6079 \text{ grm. Fe} = 0.6079 \times 0.6097 = 0.3706 \text{ grm. cane sugar in 50 c.c.}$$
or 3·764 grms. of the sugar contain 3·706 grm.
$$= \mathbf{98.47} \% \text{ cane sugar.}$$

E. COLOURING MATTERS IN DYED COTTON FABRICS

ESTIMATION OF DIRECT COTTON COLOURS ON THE FIBRE

The dyed cotton is titrated directly with an excess of
titanous chloride, which is afterwards titrated back with
iron alum.   The process is carried out in a manner similar
to the indirect method described for estimation of direct
colours in solution.

A weighed quantity of the material is placed in a
flask and first boiled with dilute hydrochloric acid.
Carbonic acid is then passed over, and an excess of titanous
chloride is run in.   The flask is heated over a Bunsen
flame until all the colour has disappeared, when it is
cooled, and the excess of titanous chloride is titrated back
with iron alum, using potassium sulphocyanide as indicator.
Generally speaking, 5 grms. of cotton are a convenient
quantity to use for each estimation, with titanous chloride
of the usual strength, 1 c.c. = 0·0015 to 0·002 grm. Fe).
Equally good results have been obtained, however, with
1·5 grm. cotton and titanous chloride made up so that
1 c.c. = about 0·0003 grm. Fe.

The method can be employed for direct cotton azo dyes, and has been proved quantitative in the case of Benzopurpurin 4B, Congo red, Erika, Chrysophenin and Brilliant yellow.

EXAMPLES.—1. 5 grms. cotton dyed with 3 % Benzopurpurin 4 B (0·15 grm.). The colour was estimated in the bath and in the fibre by the process explained above. The colour on the fibre and in solution was reduced with 50 c.c. $TiCl_3$ in each case.

Excess $TiCl_3$ found in case of fibre, 22·95 c.c.

,, ,, ,, ,, solution, 23·1 c.c. (by iron alum).

$$1 \text{ c.c. } TiCl_3 = 0·001724 \text{ grm. Fe}$$
$$= \frac{0·001724 \times 724}{448} = 0·002786 \text{ grm. Benzopurpurin}$$

$$(50 - 22·95) = 27·05 \text{ c.c. } TiCl_3$$
$$= 0·002786 \times 27·05$$
$$= 0·07536 \text{ grm. Benzopurpurin on fibre}$$

$$(50 - 23·10) = 26·9 \text{ c.c. } TiCl_3$$
$$= 0·002786 \times 26·9$$
$$= 0·07486 \text{ grm. Benzopurpurin in solution}$$

Total colour on fibre and in solution $\Big\} = 0·07536 + 0·07486$

$$= 0·1502 \text{ grm.}$$

2. 1·5 grm. cotton dyed with 0·5 % Benzopurpurin (0·0075 grm.). 25 c.c. $TiCl_3$ used in the case of fibre, and also for solution.

Excess $TiCl_3$ found in case of fibre, 16·7 c.c. (by iron alum).

,, ,, ,, ,, solution 18·9 c.c.

That is, 8·3 c.c. $TiCl_3$ used by Benzopurpurin on fibre.

,, 6·1 c.c. ,, ,, ,, in solution.

$$1 \text{ c.c. } TiCl_3 = 0·000324 \text{ grm. Fe}$$
$$= \frac{0·000324 \times 724}{448}$$
$$= 0·0005236 \text{ grm. Benzopurpurin}$$

∴ 0·0005236 × 8·3 = 0·004346 grm. Benzopurpurin on fibre

0·0005236 × 6·1 = 0·003194 ,, ,, in solution.

3. 5 grms. cotton dyed with 2 % Chrysophenin G (0·1 grm.). Colour on fibre and in solution reduced separately with 50 c.c. $TiCl_3$ in each case.

Excess TiCl$_3$ found in case of fibre 39·6 c.c., and in the case of the solution 20·8 c.c. (by iron alum).

$$1 \text{ c.c. TiCl}_3 = 0.001658 \text{ grm. Fe}$$
$$= \frac{0.001658 \times 680}{448}$$
$$= 0.002516 \text{ Chrysophenin}$$
$$(50 - 39.6) = 10.4 \text{ c.c. TiCl}_3$$
$$= 0.002516 \times 10.4$$
$$= 0.02616 \text{ grm. Chrysophenin on fibre}$$
$$(50 - 20.8) = 29.2 \text{ c.c. TiCl}_3$$
$$= 0.002516 \times 29.2$$
$$= 0.07347 \text{ grm. Chrysophenin in solution}$$

METHYLENE BLUE IN DYED COTTON FABRICS

This determination is essentially the same as the estimation of the colour itself. A known weight of the cotton is placed in a flask with water and hydrochloric acid, a current of carbon dioxide is passed into the flask, and the colour is titrated with titanous chloride. It is not always an easy matter to determine the exact point at which the dye is completely decolourized when present on the fibre, and it is consequently preferable to titrate with excess of titanous chloride, and then to titrate back with iron alum as for direct cotton colours. In this case, however, the colour acts as its own indicator, and no potassium sulphocyanide is required.

EXAMPLE.—10 grms. dyed cotton were titrated as above, and were found to require 11·15 c.c.

$$1 \text{ c.c. TiCl}_3 = 0.001563 \text{ grm. Fe}$$
$$= 0.004458 \text{ grm. Methylene blue}$$
$$\therefore 10 \text{ grms. cotton contain } 0.004458 \times 11.15$$
$$= 0.04971 \text{ grm. Methylene blue}$$
$$= \mathbf{0.497} \% \text{ Methylene blue}$$

ESTIMATION OF INDIGO IN DYED COTTON FABRICS

About 4 grms. of the dyed cotton are cut up into small pieces and placed in a porcelain beaker; 25 c.c. H_2SO_4 80 % strength (148° Tw.) are now added, and the whole is stirred slowly, the temperature being maintained at about 40° C. In a very short time the cotton begins to dissolve, and in about ten minutes it has all gone into solution. The contents of the beaker are now diluted with water to about 120 c.c. With sulphuric acid of 148° Tw. cellulose is converted into glucose, which remains in solution on diluting with water, while the Indigo is converted into a sulphate, which on diluting with water dissociates with the separation of indigotine as such. This is filtered off through a Gooch crucible containing a filtering medium of quartz and silica. It is best to use as the bottom layer quartz crushed about the size of millet seeds, then a layer of finer quartz about the fineness of grain sugar, and lastly a layer of finely divided silica. The Indigo is washed with water, and then sulphonated and titrated in the manner described for pure Indigo.

The time required for a complete estimation is a little over two hours.

EXAMPLES.—1. 4·425 grms. indigo-dyed cotton were treated by the 80 % sulphuric process, and the Indigo residue was sulphonated and titrated as described; 17·75 c.c. $TiCl_3$ were required.

$$1 \text{ c.c. } TiCl_3 = 0.001845 \text{ grm. Fe}$$
$$\text{Indigo on fibre} = \frac{0.001845 \times 262 \times 17.75}{112}$$
$$= 0.07662$$
$$= \mathbf{1.73 \%}$$

2. 3·8 grm. indigo-dyed cotton were treated by the 80 % sulphuric process, and the Indigo residue was sulphonated and titrated as described; 26·2 c.c. $TiCl_3$ were required.

$$1 \text{ c.c. TiCl}_3 = 0\text{·}001712 \text{ grm. Fe}$$
$$\text{Indigo on fibre} = \frac{0\text{·}001712 \times 262 \times 26\text{·}2}{112}$$
$$= 0\text{·}10493$$
$$= \mathbf{2\text{·}76}\,\%$$

The colours used for topping Indigo are usually either Methyl violet or Safranine, and if present will remain in solution in the sulphuric acid on diluting with water.

Of colours used for bottoming, the sulphide colours are destroyed either by the first or second treatment with sulphuric acid. Manganese bronze must be removed from the fibre with bisulphite of soda and sulphuric acid. Diamine black B.H. dissolves in 80 % sulphuric, and appears to be precipitated on diluting. In sulphonating, however, the colour is destroyed, and gives a brown precipitate on diluting. This substance does not, however, affect the accuracy of the Indigo estimation. Columbia black and Benzopurpurine 4B are apparently not destroyed in the sulphonating process, but are completely precipitated on diluting with water, so that they can be easily separated by filtration before titrating. Other colours, like Diamine sky blue and Diaminogene are to some extent soluble in acid, and if not detected may give rise to erroneous results. In case direct cotton colours have been detected in the preliminary examination of the dyed fabric, the safest plan to adopt is to wash the precipitated indigo, after filtration with dilute ammonia, when any direct cotton colour will at once be rendered completely soluble, and will be carried into the filtrate. Thio-indigo red and other vat dyes such as Ciba blue, Indanthrene blues, the Algoli colours, etc., do not sulphonate with ordinary sulphuric acid, and if present in the fabric would consequently not interfere with the volumetric estimation of the indigotine.

ESTIMATION OF THE DEGREE OF MERCERIZATION IN COTTON YARNS.[1]

If the yarn is dyed, the colour should be previously stripped by suitable means, *e g.* by treatment with acid and then with soda (mordant dyes), or by means of bleaching powder (basic and sulphide colours) or of titanous chloride (azo dyes).

The weighed sample of cotton under investigation (from 1 to 5 grms.) is dyed together with a weighed quantity of ordinary bleached cotton yarn by boiling for about 20 minutes in a bath containing Benzopurpurin 4B in excess, and after rinsing slightly the amounts of colour taken up by each are then estimated by the method detailed above. The figures obtained are compared with those given in the table below; these must, however, not be regarded as absolute, but as proportional values. Thus it may be found that in this determination the ordinary cotton has taken up less than 1·77 % of colour (the concentration of the dye liquor being the main contributing factor), and it therefore becomes necessary to calculate by proportion, from the amount of colour found on the ordinary yarn and that under examination, how much colour the sample would have absorbed if the amount taken up by the ordinary cotton was 1·77 %.

EXAMPLE.—5 grms. ordinary and 5 grms. mercerized cotton yarn were dyed in one bath with 4 % Benzopurpurin 4B. The samples were then taken out, rinsed slightly, and the colour estimated in each. The ordinary yarn was found to contain 1·405 % colour, and the mercerized 2·628 %.

If the ordinary yarn had taken up 1·77 % colour, then, by simple proportion, the mercerized yarn would have

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[1] *Journ. Soc. Dyers and Col.*, 1908, p. 68.

taken up 3·31 %. By reference to the table, it is seen that the mercerized yarn had been treated with caustic soda of about 50° Tw. strength.

Table showing the amounts of Benzopurpurin 4B taken up from the same bath by ordinary cotton and by cotton mercerized under tension in different strengths of caustic soda.

Strength of caustic soda.	Amount of colour taken up.	Strength of caustic soda.	Amount of colour taken up.
Untreated	1·77 %	45° Tw.	3·27 %
10° Tw.	1·88 ,,	50° ,,	3·38 ,,
20° ,,	2·39 ,,	55° ,,	3·50 ,,
25° ,,	2·57 ,,	60° ,,	3·56 ,,
30° ,,	2·95 ,,	65° ,,	3·60 ,,
35° ,,	3·02 ,,	70° ,,	3·66 ,,
40° ,,	3·15 ,,		

It should be noted that the figures given in the table only apply to cotton yarn mercerized *under tension.* If the mercerizing has been done without tension, the amounts of Benzopurpurin taken up are considerably greater. It is furthermore important to bear in mind that mercerized cotton, when dried at an elevated temperature, loses much of its characteristic affinity for colouring matters.[1] It is probably on this account that the above-mentioned process (likewise the iodine test) usually fails to give reliable results when applied to mercerized cotton piece goods, since these are generally dried over steam-heated cylinders, and are thus exposed to temperatures which materially alter the affinity of the fibre for colouring matters.

[1] *Journ. Soc. Dyers and Col.*, 1908, p. 107.

PART IV

TUNGSTEN AND MOLYBDENUM

TUNGSTIC and molybdic acids are reduced by titanous chloride, but it was not found possible to estimate them by means of this reagent, as no definite end-point could be obtained. Chromic salts [1] are apparently not acted upon at all by titanous chloride. All these metals can, however, be reduced by means of zinc and hydrochloric acid to definite compounds, which, when treated with suitable oxidizing agents, give well-defined end reactions.

Tungsten.—As is well known, tungstic acid is reduced to the condition of $WoCl_4$ by energetic reduction with granulated zinc and hydrochloric acid. Otto von der Pfordten [2] has utilized this reaction for the quantitative estimation of tungsten, titrating the reduced solution with permanganate in presence of manganous sulphate. The appearance of a pink colour is coincident with the oxidation back to tungstic acid.

In the new method the same reactions are relied upon, but iron alum is chosen as the oxidizing agent, with potassium sulphocyanide as indicator. The titration is thus rendered possible in presence of salts of iron, and can be conducted in even strong hydrochloric acid solution.

[1] The salts of chromic acid have already been dealt with (see pp. 16 and 58).

[2] *Berl. Ber.*, 1883, p. 508.

The reaction takes place according to the equation—

$$WoCl_4 + 2FeCl_3 = WoCl_6 + 2FeCl_2$$
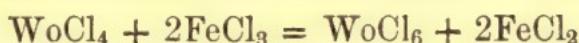
The method was tried in the first place on pure dry tungstic acid, the purity of which was ascertained by reducing a known weight in a current of pure dry hydrogen at a temperature of about 600° C.

0·5320 grm. of tungstic acid gave 0·4220 grm. metallic tungsten. The amount required by theory is 0·4219 grm. A known weight of this product was now dissolved in ammonia, the solution acidulated with strong hydrochloric acid and reduced with pure granulated zinc in a flask through which a current of carbon dioxide was maintained.[1] The solution thus obtained was titrated with standard iron alum in presence of potassium sulphocyanide, and gave 99·69 % WoO_3.

A pure recrystallized tungstate of soda ($Na_2WoO_4 + 2H_2O$) titrated in the same way gave the following result :—

	Found.	Calc.
Na_2WoO_4	89·36 %	89·06 %
Water of cryst.	10·72 ,,	10·94 ,,
	100·08 ,,	100·00 ,,

In the reduction of the tungstic acid, the colour of the solution almost immediately becomes dark blue, which after a short time becomes fainter and ultimately changes to a distinct brown, this marking the end of the reaction. If iron alum is now run into this solution without any sulphocyanide being present, the brown colour changes to blue, and by further additions this ultimately disappears, leaving a colourless liquid, which is rendered milky by the presence of white precipitated

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[1] If this precaution is not taken, the $WoCl_4$ very readily suffers oxidation by contact with the air, and the results consequently come out low.

tungstic acid. The disappearance of the blue exactly coincides with the formation of the red when suphocyanide is used as indicator. It is possible, therefore, to dispense altogether with the use of potassium sulphocyanide as indicator.

EXAMPLE.—One gram of commercial *tungstate of soda* was dissolved in water and the solution made up to 100 c.c.

10 c.c. of this solution were reduced in a flask with a large excess of concentrated hydrochloric acid and pure granulated zinc until the brown colour was obtained. The reduced solution was titrated with iron alum until the blue colour disappeared. 17·1 c.c. iron alum were required.

$$1 \text{ c.c. iron alum} = 0\cdot001891 \text{ grm. Fe}$$
$$294 \text{ Na}_2\text{WoO}_4 = 112 \text{ Fe}$$
$$\therefore 1 \text{ c.c. iron alum} = 0\cdot004963 \text{ grm. Na}_2\text{WoO}_4$$
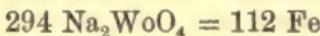
and 10 c.c. sodium tungstate solution contain—

$$0\cdot004963 \times 17\cdot1 = 0\cdot08486$$
$$= \mathbf{84\cdot86}\%$$

Molybdenum.—By energetic reduction with zinc and hydrochloric acid, molybdic acid and its salts can be reduced to the condition of $MoCl_3$. This compound can be reoxidized by permanganate and other oxidizing agents to the condition corresponding to molybdic acid.

Attempts to base a method of estimating molybdenum upon reduction with zinc and hydrochloric acid, and subsequent titration with iron alum in presence of potassium sulphocyanide proved unsuccessful, since the indicator forms with the reduced molybdenum compound an intensely coloured sulphocyanide which quite obscures the end-reaction with the ferric salt.

A definite end-point was, however, obtained by titrating the reduced molybdenum solution with a standardized solution of Methylene blue.[1] The colour of the former

[1] *Knecht and Atack.*

changes from salmon-pink to straw-yellow, then to pale apple-green (due to the formation of $MoCl_5$), and ultimately to the characteristic shade of Methylene blue, this indicating the end-point of the reaction. In this case the oxidation of the $MoCl_3$ does not proceed as far as molybdic acid, as is the case when permanganate is used as the oxidizing agent, but only as far as $MoCl_5$. As soon as the oxidation has proceeded far enough to complete the formation of $MoCl_4$, the pale green colour characteristic of the $MoCl_5$ makes its appearance. To obtain the blue colour, exactly twice the volume of Methylene blue has to be added, so that the reaction takes place in two distinct stages—

$$2MoCl_3 + 2HCl + O = 2MoCl_4 + H_2O$$
$$2MoCl_4 + 2HCl + O = 2MoCl_5 + H_2O$$
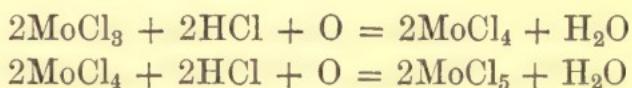
in which the Methylene blue takes the part of the oxidizing agent.

The method was tested on a pure molybdate of ammonia, which was found by the gravimetric method (estimation as lead molybdate) to contain 54·4 % Mo, the amount calculated for the formula $(NH_4)_6Mo_7O_{24} . 4H_2O$ being 54·36 %.

By direct titration with Methylene blue, the following figures were obtained: 54·36; 54·43; 54·39; 54·49 % in different estimations.

The method was also tested on pure molybdic acid, which, when dissolved in ammonia, reduced with zinc and hydrochloric acid, and then titrated with Methylene blue, gave 66·60 % Mo against 66·66 % required by theory.

In all reductions, likewise in the titrations, the reduced molybdenum solution must be kept out of contact with the air, and this is most conveniently effected

by passing a current of carbon dioxide through the flask containing the solution. If this precaution is not observed, the results will inevitably come out too low, as is evident from the result of the following experiment :—

A reduced solution of ammonium molybdate titrated as described gave Mo = 54·42 %. In a second experiment, air was drawn for fifteen minutes through the flask containing the reduced solution. The amount of molybdenum found by titration was then only 44·30 %.

The most suitable strength of Methylene blue solution for use in these titrations is $\frac{N}{40}$, or one containing approximately 4 grams per litre. It is standardized by means of titanous chloride (see p. 80).

For completing the reduction of the molybdenum solution, the apparatus described on p. 52 may be employed with advantage.

EXAMPLE.—0·8 grm. of molybdic acid was dissolved in caustic soda and the solution made up to 100 c.c.

10 c.c. of this solution were transferred to a flask, and after adding a large excess of concentrated hydrochloric acid, the reduction was brought about by the addition of zinc. When the reduction was complete (which is indicated by the solution acquiring a salmon-pink colour), it was titrated with Methylene blue to the appearance of the blue colour. 25·55 c.c. Methylene blue were required.

1 c.c. Methylene blue = 0·002068 grm. Mo

10 c.c. molybdic acid solution contain—

$$0·002068 \times 25·55 = 0·05283 \text{ grm. Mo}$$
$$= 66·35 \% \text{ Mo}$$

Chromium.—When chromates or chromic salts are reduced with zinc and hydrochloric acid, they give rise to blue chromous chloride, $CrCl_2$. It is highly probable that this salt reacts with a ferric salt in the following manner :—

$$CrCl_2 + FeCl_3 = CrCl_3 + FeCl_2$$
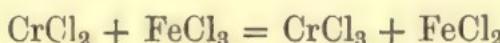
Attempts were made to utilize this reaction for estimating chromium, but failed in consequence of the chromous chloride immediately beginning to revert to chromic chloride with evolution of hydrogen. The results were consequently far too low. Using chemically pure bichromate of potash as standard, the reduction was effected in a cylindrical tap funnel closed at the top with an indiarubber stopper provided with a Bunsen valve. Although the reduced solution was run straight into excess of iron alum contained in a flask through which a current of carbon dioxide was maintained, the highest result obtained was 97% $K_2Cr_2O_7$. The method is therefore of no practical value.

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INDEX TO SUBJECTS

THE END